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A thermodynamic analysis of a proposed power plant to mitigate carbon dioxide emissions

William Lowery Martin

To the Graduate Council:

I am submitting herewith a thesis written by William Lowery Martin entitled "A thermodynamic analysis of a proposed power plant to mitigate carbon dioxide emissions." I have examined the final electronic copy of this thesis for form and content and recommend that it be accepted in partial fulfillment of the requirements for the degree of Master of Science, with a major in Mechanical Engineering.

Mancil Milligan, Major Professor

We have read this thesis and recommend its acceptance:

Accepted for the Council:
Carolyn R. Hodges

Vice Provost and Dean of the Graduate School

(Original signatures are on file with official student records.)

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Acceptance for the Council:

Vice Provost and Dean of
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A THERMODYNAMIC ANALYSIS OF A PROPOSED POWER PLANT TO MITIGATE CARBON DIOXIDE EMISSIONS

A Thesis
Presented for the
Master of Science
Degree
University of Tennessee, Knoxville

William L. Martin
December 2003

DEDICATION

This thesis is dedicated to my family, who provided me the freedom, opportunity and support to go to graduate school. My mom, Marky Martin; my uncle and aunt, Bill and Diana Lowry; and my grandmother, Ouida Lowry, all made achieving a post graduate degree a much easier pursuit than it should have been. The support all of you provided during this effort made this thesis a reality. Thank you and I love you all.

ACKNOWLEDGEMENTS

I owe this thesis to a lot of people who helped me a lot more than I could have possibly asked or imagined. First and foremost, my family, to whom this thesis is dedicated, provided invaluable financial support and general encouragement through the process of finishing this work. It would not have happened without them.

Further thanks are due to several members of the Mechanical, Aerospace and Biomedical Engineering Department: Dr. Tom Shannon, department head; Dr. Gary Smith, head of the graduate committee; Dr. Mancil Milligan, head of my committee; and Dr. Stan Johnson and Dr. Masood Parang, other members of my committee. The professionalism these men displayed and the help, encouragement, guidance and support each of these men provided in their roles throughout this process kept me going and always gave me hope that there was a light at the end of the tunnel. I will never forgot their willingness to help me reach my goal of finishing my degree and I will never be able to work off the debt of gratitude I owe to each of them for the degree I have.

Dr. Fred Weber of the Chemical Engineering Department gave me access to the HYSYS software and operating manuals to learn how to apply it to my work. This software is an integral part of my study and his service in making sure I could continue to use this tool to complete my thesis deserves more thanks than I can express.

The time that many different men in industry gave to helping me include current data in my models helped me to have confidence in the work I did. I value the knowledge that they shared with me during the process of putting this work together. Their graciousness in reviewing my work to ensure that the theory in it is mixed with practicality added greatly to the final product.

To all the friends who made sure I continued to enjoy life and to grow spiritually during graduate school, thank you. The support and accountability you provided in this work and many other things served me well. You all know who you are.

Of course, none of this would be possible without the gifts given to me by my Father in Heaven and the lavish grace He so freely gives. All the praise truly goes to Him.

ABSTRACT

One of the major issues surrounding energy generation and use is the impact it has on the global climate Any process that includes the combustion of fossil fuels, such as coal, oil and natural gas, contains carbon dioxide among its exhaust products. The natural greenhouse effect is what makes the earth habitable, but if it is intensified by increased carbon dioxide concentration in the atmosphere, it may cause changes in global temperature, growing seasons or weather patterns that will alter the way of life for many people. The fact that carbon dioxide concentrations have increased by around 30 percent since the dawn of the industrial revolution has been shown by numerous studies.

Because energy has such a central role in the global economy it is no simple matter to change the method of producing it. The infrastructure and technology in use today is geared toward the combustion of fossil fuels. Therefore, it seems logical to plot a path forward that uses fossil fuels in the generation of power while finding a way to mitigate the carbon dioxide emissions from such a process. The proposed MATIANT cycle is one way of meeting both these criteria. This process uses natural gas as its fuel, but allows for the removal of a carbon dioxide stream from the process, which can then be sequestered by any number of methods.

In addition to using well established technology, any new method of generating power much provide a performance equal to that of conventional systems. This thesis analyzes the MATIANT cycle on a technical basis to determine if it is a feasible alternative to producing power. A model of the cycle is built using HYSYS process simulation software and then investigated for fuel use, efficiency and power output. These findings are compared the performance of a traditional power plant that has statepoints similar to those of the MATIANT cycle, such as maximum cycle pressure and temperature. In addition, the individual component performance of the MATIANT cycle is studied in order to gain a better understanding of the process. Furthermore, the MATIANT cycle is subjected to a parametric study whereby certain statepoints in the process are changed to gain an appreciation of their impact on cycle performance. The results of these parametric studies are compared to the base case MATIANT cycle performance.

The parametric studies reveal that first law efficiency increases as the maximum cycle temperature increases and decreases as intercooler exit temperature increases. These parameters both have a more significant impact on the performance of the MATIANT cycle than changes in oxygen delivery temperature, fuel pressure or maximum cycle pressure. Cycle performance can be enhanced by adding an extra stage of compression and by eliminating the air separation unit powered by the MATIANT cycle. Compared to a simple cycle with similar process statepoints, the MATIANT cycle has a significantly higher first law efficiency, but the second law efficiency is appreciably lower. A component by component analysis of the MATIANT cycle reveals that the combustion chambers contribute the most irreversibility to the process, while the compressors are the least efficient components. A large amount of work is destroyed in

the intercoolers, but they are useful to remove water from the process and to lower the compression power. Although further work on the MATIANT cycle is warranted, including a detailed economic analysis, this work proves that there is a technical basis to accepting the MATIANT cycle as an alternative to conventional power generation.

PREFACE

Energy plays a vital role in the way the world does business and enjoys leisure. The process of providing that energy to the world in a useful form is a dynamic process, as new challenges give birth to new discoveries and inventions to continue to meet the world's energy needs. This work addresses just one solution to one challenge facing the world in the field of power generation and attempts to provide a deeper understand of this solution in comparison to current practices. It is only by fully understanding the new inventions that they can be adequately and usefully applied.

TABLE OF CONTENTS

LIST OF TABLES

LIST OF FIGURES

NOMENCLATURE

Symbols

atma	Atmospheres (absolute)
bara	Bar (absolute)
Btu	British thermal units
C	Carbon
CH_4	Methane
CO_2	Carbon Dioxide
COMPOSITION	Composition of a stream
c_p	Constant pressure specific heat
^oC	Degrees Celsius
$\frac{dE}{dt}$	Time Rate of change in the energy of a control volume
$\frac{dS}{dt}$	Time rate of change in the entropy of a control volume
^oF	Degrees Fahrenheit
g	Acceleration due to gravity
H_2O	Water
h	Molar enthalpy
HHV	Higher heating value
hp	Horsepower
hr	Hours
$\dot{I}$	Flow rate of irreversibility
k	Specific heat ratio
K	Kelvin
kg	Kilograms
kgmol	Kilogram moles
kgmol/hr	Kilogram moles per hour
kgmol/s	Kilogram moles per second
kJ	KiloJoules
kJ/kgmol	KiloJoules per kilogram mole
kJ/kgmol-K	KiloJoules per kilogram mole Kelvin
kPaa	Kilopascals (absolute)
kW	KiloWatts
kWh	KiloWatt hours
lbmol	Pound-moles
m	meters
m^3	Cubic meters
M	Mega (million)
MJ	MegaJoules
MMBtu	Millions of Btu
MW	MegaWatts

$\dot{n}$	Molar flow rate
N_2	Nitrogen
NO_2	Nitrogen Dioxide
O_2	Oxygen
P	Pressure
ppb	Parts per billion
ppm	Parts per million
psia	Pounds per square inch (absolute)
$\dot{Q}$	Energy flow due to heat transfer as a function of time
s	Molar entropy
T	Temperature
V	Velocity
$\dot{W}$	Energy flow due to work as a function of time (power)
z	Elevation from a predetermined datum
%	Percent

Greek Symbols

α	Heat rate
ε	First law efficiency
η	Second law efficiency
ψ	Flow rate of availability
$\dot{\sigma}$	Flow rate of entropy generation

Subscripts

1, 2, 3, …	Stream 1, 2, 3, etc. in a control volume
chemical	Refers to the chemical contribution to a value
comb	Refers to the contribution of combustion to a value
comp	Relates a value to the compressor
e	Value of a property at the exit of a control volume
fuel	Relates a value to the fuel
HHV	Relates a value to the higher heating value
i	Value of a property at the inlet of a control volume
max	Maximum
min	Minimum
net	Refers to the total amount of a value in a control volume
o	The dead state value of a property
poly	Polytropic
products	Refers to the products of a combustion process
reactants	Refers to the reactants of a combustion process
thermomechanical	Refers to the temperature and pressure contribution to a value

total	Refers to the total amount of a value
turb	Relates a value to the turbine

Chapter 1. Introduction

Section 1.1. Energy: Current Status and Projections. Everywhere one looks the use and impacts of energy are obvious. Because of energy, it is possible to stay cool in the summer and warm in the winter. It also increases entertainment and learning options through media such as radio, television and the Internet. Furthermore, it allows for easier storage, access and dissemination of information as well as swifter and more convenient forms of travel. The benefits of energy can be summarized by saying that it enhances the quality of life of its users.

Because of its many positive effects, energy consumption continues to rise. According to the Energy Information Administration (EIA) [1], worldwide energy consumption increased by almost 85 percent between 1970 and 1999 and an additional rise of 59 percent is expected between 1999 and 2020. As Table 1.1 from the EIA International Energy Outlook shows, much of this growth is expected to occur in developing countries.

Population is a factor in these increases, although not the sole factor. The aforementioned ability of energy to increase the quality of life in the developing regions to match that of the industrialized countries is also a major driver in the increase in energy consumption. The World Energy Council [2] states that in 1990, about three-fourths of the world's population lived in developing countries but consumed only one-third of the world's energy production. It is believed that by 2020 85 percent of the world will live in developing regions while consuming 55 percent of the energy generated. The trend predicted in this statement is that energy use in the developing

Table 1.1. World Energy Consumption, 1990-2020

Region	Energy Consumption (Quadrillion Btu)			
	1990	1999	2010	2020
Industrialized Countries	182.4	209.6	243.4	270.4
Eastern Europe/Former Soviet Union	76.3	50.5	60.3	72.3
Developing Countries	87.2	121.8	186.1	264.4
Total	346.0	381.8	489.7	607.1

world will outstrip population growth, supporting the fact that it is not the sole driver of increased energy use.

While the technology for energy production may differ, most of the world generates its energy using fossil fuels—coal, oil or natural gas. Figure 1.1 shows the 1990 breakdown of the sources of the world's energy as given by the World Energy Council [3], with fossil fuels responsible for 77 percent of energy consumption.

The EIA [4] discloses that in the United States fossil fuels account for 84 percent of energy production in 1999. Forecasts to 2020 by the EIA [5] predict that the overall use of fossil fuels will increase and take a larger role in worldwide energy consumption, with natural gas surpassing coal as the second most popular fossil fuel behind oil.

A substantial portion of the consumption of energy is in the form of electricity by commercial, industrial and residential users. The EIA [6] estimates that electricity production by electric utilities consumes 36 percent of the energy produced in the United States, with coal accounting for 56 percent of this figure. As Figure 1.2, taken from the EIA International Energy Outlook reveals, more than two-thirds of the total electricity used in the United States, including utilities and other sources of electricity, comes from fossil fuels.

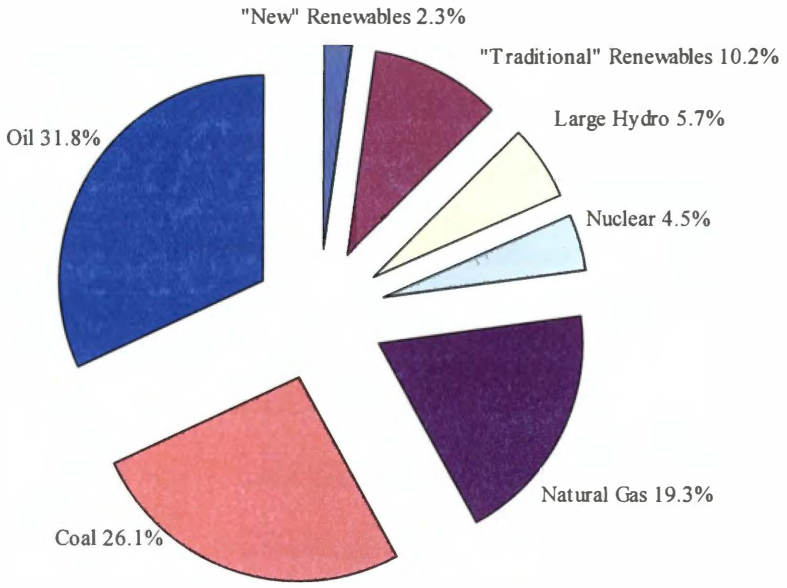

Figure 1.1. World Energy Use, 1993

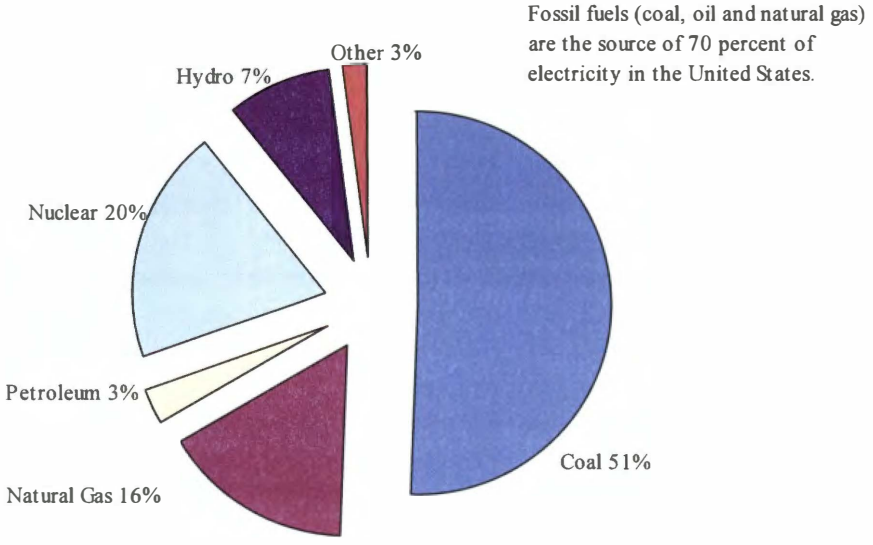

Figure 1.2. US Energy Consumption by Electricity

As will be shown in a later section, it is impossible to separate energy consumed from environmental effects. The National Pollution Prevention Center [7] states, "The health and welfare of human populations is closely linked to the state of the environment." From the environment, societies obtain resources; however, human health and well being are integrally linked with a healthy environment. In addition, economics are closely related to the environment in that it provides the resources and energy that are used in industry and business. Therefore, it stands to reason that potential environmental impacts should play a vital role in any decision that a society makes, including methods of producing energy. This thesis will focus on the analysis of a power plant that generates power in a manner that is respectful of the environment by allowing for a carbon dioxide stream to be captured and then sequestered rather than being exhausted to the atmosphere.

Section 1.2. The Greenhouse Effect and Global Warming. One of the most deleterious effects of energy production by fossil fuels is enhancing the greenhouse effect. While not inherently bad, the greenhouse effect is capable of inducing large-scale planetary changes due to the global warming it causes. The natural greenhouse effect is a phenomenon that is necessary for the earth to support life. Incoming shortwave solar radiation passes uninhibited through the atmosphere while outgoing longwave radiation emitted by the earth is trapped, much like a greenhouse. Thus, the occurrence of the natural greenhouse effect serves to make earth habitable by maintaining an average surface temperature of 15°C (59°F). Without the natural greenhouse effect, most energy from the sun incident upon the earth would be emitted back into space rather than trapped in the atmosphere, making the earth too cold for habitation.

The greenhouse effect occurs because certain trace gases in the atmosphere trap heat radiating from the earth's surface, warming the atmosphere. Gases that cause the greenhouse effect are known as greenhouse gases: carbon dioxide, methane, tropospheric ozone, nitrous oxide and chlorofluorocarbons. Of these gases, human activities create carbon dioxide in the largest amounts, primarily by combusting fossil fuels. Worldwide, anthropogenic emissions of carbon dioxide total 6000 Megatons per year, by far the largest man-made greenhouse gas. Figure 1.3, based on data from the National Pollution Prevention Center [8], shows the breakdown of human production of greenhouse gases.

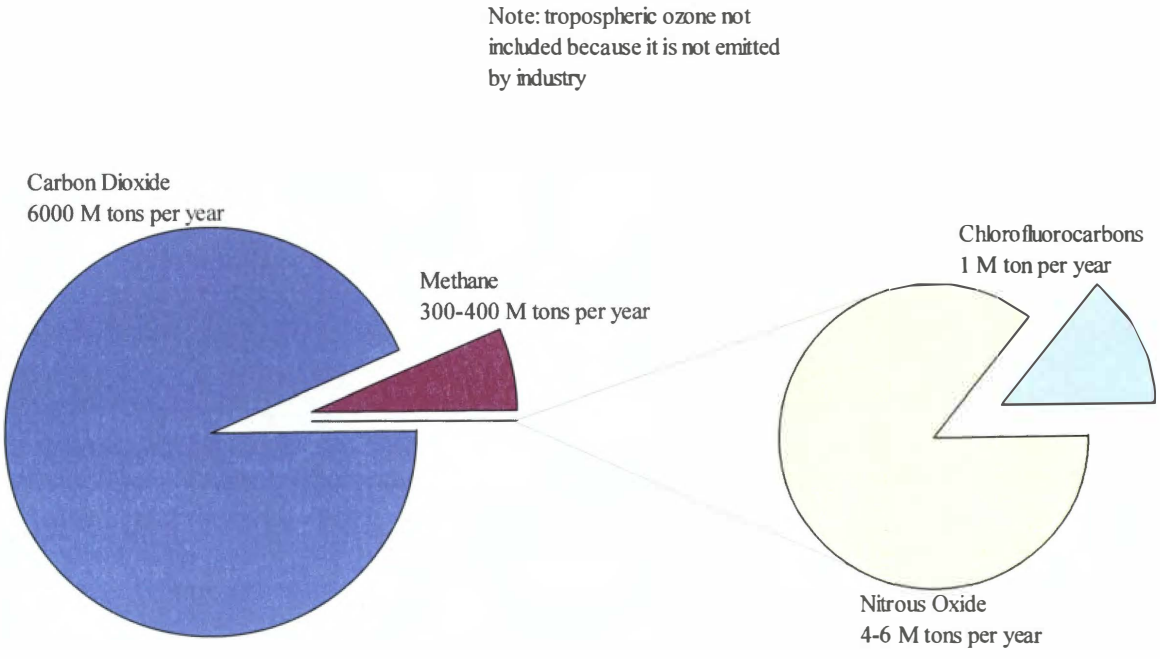

Figure 1.3. Worldwide Anthropogenic Emissions of Greenhouse Gases

Carbon dioxide can reside in the atmosphere for up to 200 years. Consequently, carbon dioxide buildup in the atmosphere is not solely due to present activities but also to past activities. By the same logic, today's actions could still be felt far into the future, beyond the lifetime of anyone alive today. Several facts serve to highlight the impact that human activities are having on the amount of carbon dioxide stored in the atmosphere. According to the Intergovernmental Panel on Climate Change (IPCC), atmospheric carbon dioxide concentrations remained relatively constant at 280ppm from 1000A.D. to 1750. This is based on the analysis of Antarctic ice core samples entrained with air. IPCC research shows that the current atmospheric carbon dioxide concentration is 380ppm, a rise of 31 percent since 1750 [9]. Furthermore, the Nova Program "What's Up with the Weather?" [10] reports that over the past 100 years, the average surface temperature of earth has risen 0.6°C (1°F). While this may not seem like a large increase, temperature records again gained from ice core samples indicate that it stands out over the past 1000 years as an appreciable rise. In an effort to discern whether the temperature variation was natural or manmade, the IPCC ran computer simulations that both included and ignored the potential anthropogenic effects on the climate. Some natural occurrences advanced to explain the rise in carbon dioxide levels include solar fluctuations and volcanic activity. The models that accounted for humans' perceived contributions to the temperature rise closely agreed with observed data. From the evidence, the IPCC's Second Assessment Report, released in 1995 [11], concluded, "The balance of evidence suggests a discernible human influence on the global climate." The third assessment report [12], released in 2001, went even further by saying "There is new and stronger evidence that most of the warming observed in the last fifty years is attributable to human activities." The following

graphs will lend credence to this claim. Figure 1.4, taken from a section of Nova's website dedicated to "What's up with the Weather?" shows the increase in atmospheric carbon dioxide concentration since the late 1950s [13] and Figure 1.5 shows that the global temperature has increased from the previous mean by almost 1°F since 1880 [14]. Looking at the last thirty years of Figure 1.5 in particular, a steady upward trend is observed that correlates with the upward trend in atmospheric carbon dioxide concentration in the last forty years.

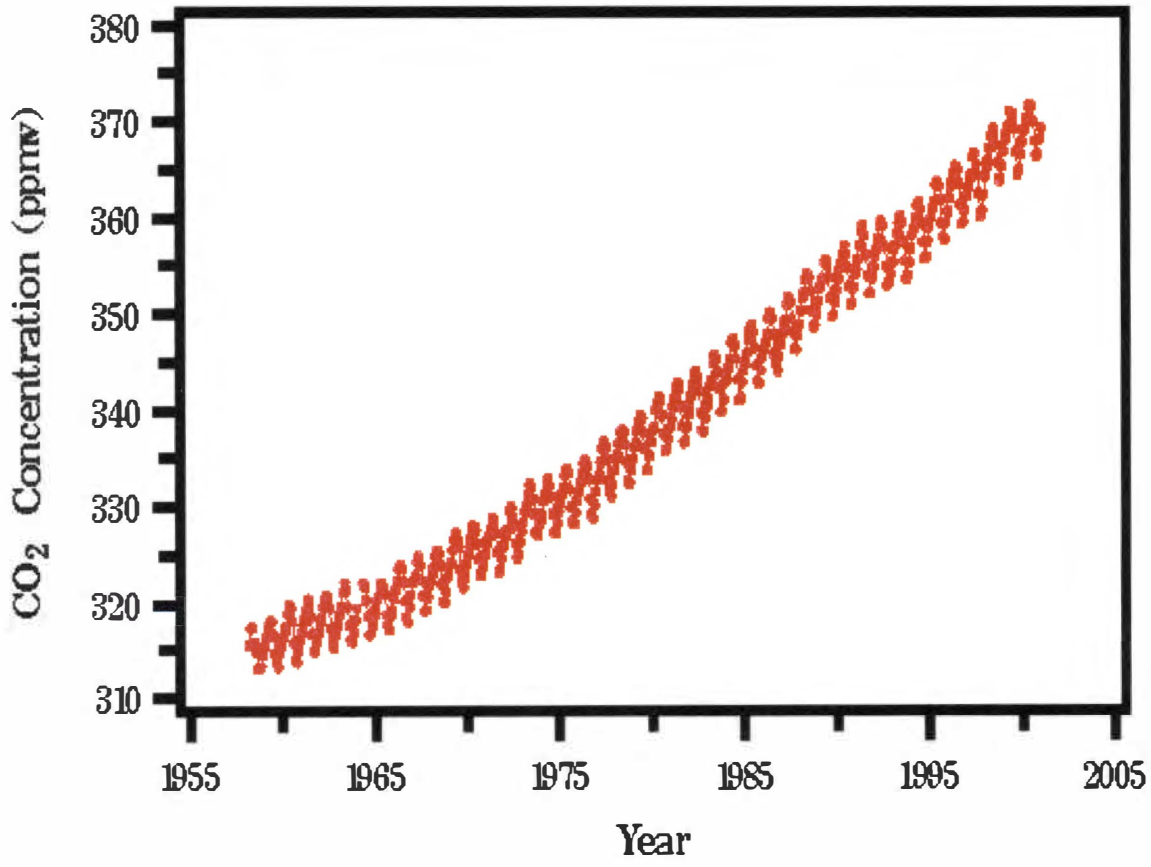

Figure 1.4 Atmospheric Carbon Dioxide Concentration Since 1955

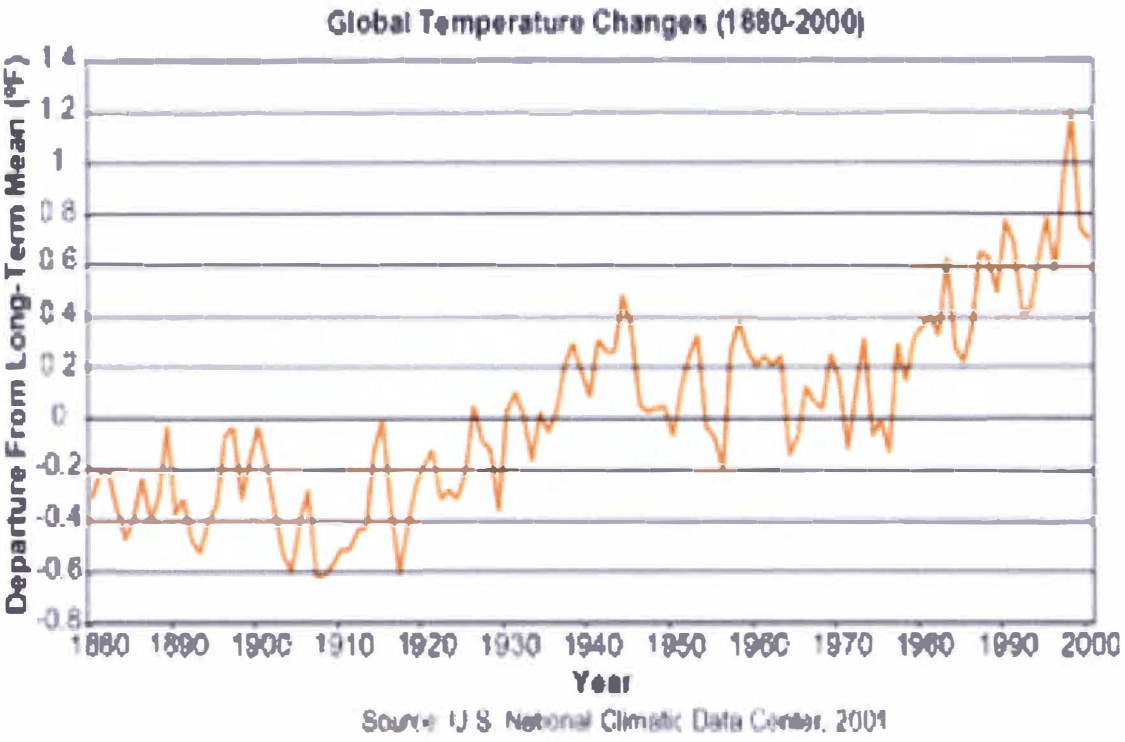

Figure 1.5. Temperature Departure from Base Case Since 1880

While the previous two figures are instructive, they are not conclusive because they do not provide a complete picture of the historical climate record. It is possible that the correlation shown is merely a coincidence, with rising temperatures corresponding to increasing atmospheric carbon dioxide concentration due to unrelated events. Figure 1.6, from the online summary of the Nova program [15] attempts to debunk the claim that increases in carbon dioxide concentration and temperature are not related.

Using temperature and carbon dioxide records from Antarctic ice dating back to 160,000 years before the present, the graph depicts an unmistakable connection between changes in global temperature and atmospheric carbon dioxide. Based on the previous three figures, the connection between atmospheric carbon dioxide and surface temperature is undeniable: continuing to emit carbon dioxide to the atmosphere will lead

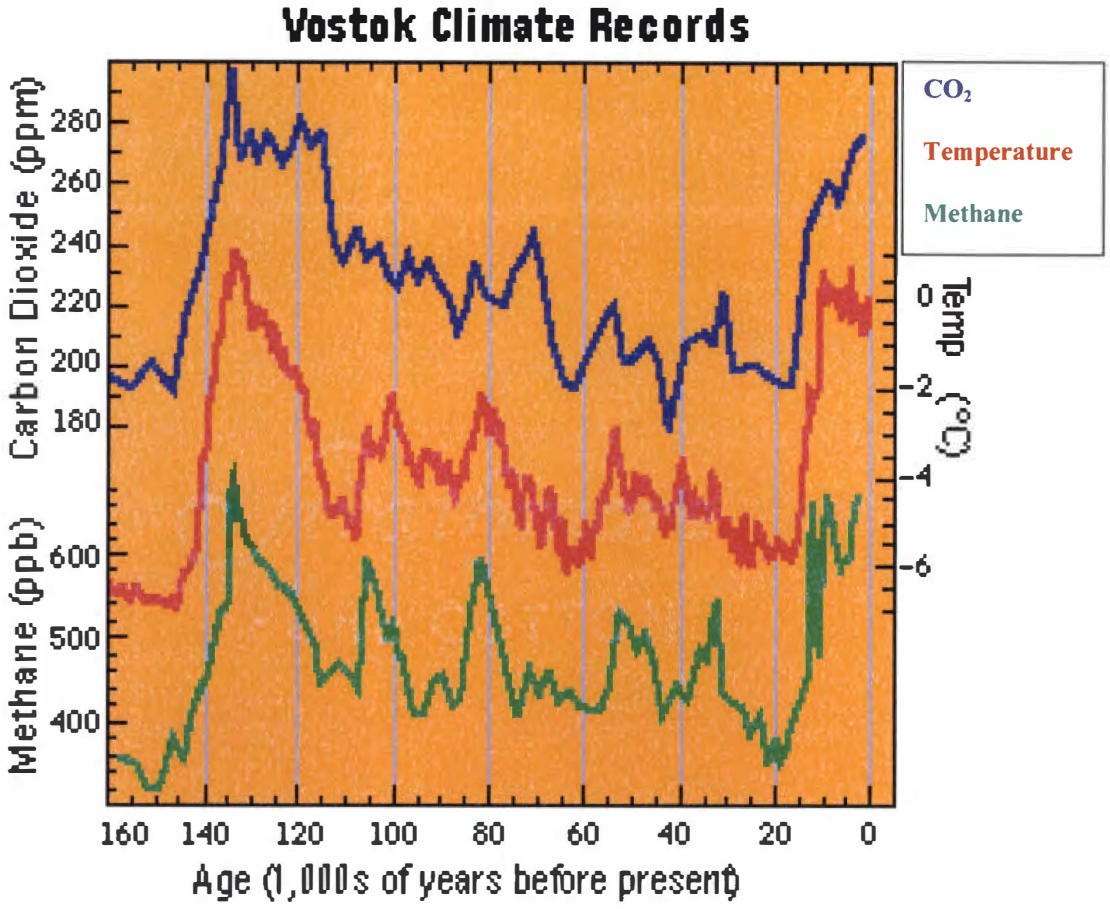

Figure 1.6. Historical Record of Temperature and Atmospheric Carbon Dioxide Concentration

to a temperature increase on earth.

Due to the fact that carbon dioxide has long residence times in the atmosphere, the current trends of increasing atmospheric concentration can be predicted to continue. The IPCC [16] claims that levels could be as high as 1260ppm by 2100 if energy use and generation trends continue. Accompanying this claim is one that says the average surface temperature of the planet could rise by as much as 5.8°C. Courtesy of the EIA [17], Table 1.2 shows projected increases in carbon emissions.

Table 1.2. World Carbon Emissions, 1990-2020

Region	Carbon Emissions (10^6 Metric Tons)			
	1990	1999	2010	2020
Industrialized Countries	2842	3122	3619	4043
Eastern Europe/Former Soviet Union	1337	810	940	1094
Developing Countries	1641	2158	3276	4624
Total	5821	6091	7835	9762

It can be seen that the developing countries and EE/FSU are the main contributors to the rise, much as they are believed to be overtaking the industrialized nations in energy consumption. The problem is serious enough that in December 1997, almost 100 nations met in Kyoto, Japan, to discuss reducing net emissions of certain greenhouse gases, primarily carbon dioxide. The nations that met in Kyoto were part of the United Nations Framework Convention on Climate Change adopted in 1992. The result of this meeting was the Kyoto Protocol, which dictated cuts in carbon dioxide emissions to below 1990 levels. The document sought to set carbon dioxide emissions in most industrialized countries at a level five percent below 1990 levels. The United States was asked to cut carbon dioxide emissions seven percent below 1990 levels. Although signed by the United States, the Senate voted not to ratify it by a vote of 95-0, meaning that it did not go into effect [18].

Current scientific thought leaves little doubt that the activities of man have led to an increase in the atmospheric concentration of greenhouse gases, most notably carbon dioxide. Furthermore, it is accepted that the significant temperature rise observed over the last century is directly related to the increase in atmospheric carbon dioxide. In spite

of the consensus on the impact of human activities and their effect on global temperatures, agreement has not been reached on the impacts of the temperature change. Thermal expansion and melting ice caps will cause world sea levels will rise, although the IPCC [19] is uncertain of the exact magnitude of the rise, giving a range of 0.09 to 0.88 meters (.3 to 2.9 feet) by 2100 in its third report. More intense precipitation events and maximum cyclone winds are also believed to be likely. Of less certainty are effects on ocean currents and cloud formation. A change in ocean currents could lead to a reduction in heat transport to high latitudes, lessening the effects of global warming in places. In addition, the type of cloud that is formed by the increased evaporation caused by global warming could mitigate the warming or even have a net cooling effect. Some perceive global warming to be a positive thing, enlarging the area and lengthening the season for growing crops and leading to fewer deaths due to extreme cold and a reduction in some diseases. On the other hand, global warming could increase the number of heat related deaths around the world, decrease crop yields, lower the amount and quality of water supplies and increase the range of certain diseases.

Uncertainty is inherent in any prediction or extrapolation. In the case of global warming, there are too many unknowns to unequivocally assert what the impacts of the rising global temperature will be. The IPCC [20] admits further study is required to reconcile current gaps in information and understanding. As stated before, the specific effects are secondary to the fact that the cause is real: man is causing the earth to heat up. The point of this thesis is not to give credence to any one of these theories, nor does it endeavor to propound a new theory as to what events will accompany global warming. An additional complication is that global warming can be perceived as a long- term

problem. Energy consumption makes life better today while the problems it brings will not be felt until tomorrow. Compared to other problems caused by burning fossil fuels such as acid rain and smog, global warming seems a long way off. However, IPCC evidence suggests that global warming is not a long way off but is happening right now. It also asserts that without some sort of immediate intervention, the problem will accelerate and intensify. Knowing that the earth is presently habitable and recognizing that a majority of environmental scientists believe that the continued increases in carbon dioxide output will have negative effects on the environment and global climate, the goal of this thesis will be to assess a power generation cycle that is designed to have a pure carbon dioxide stream that can be captured rather than emitted to the atmosphere, thus mitigating the negative impact power generation can have on the environment.

The National Pollution Prevention Center [21] indicates that carbon dioxide is the largest contributor to the anthropogenic greenhouse effect, causing as much as 50 percent of global warming. Figure 1.7 displays a breakdown of how much each greenhouse gas contributes to global warming.

Due to its prominent place in the anthropogenic greenhouse effect, carbon dioxide emissions are a logical starting point to combat the problem. Figure 1.3 through Figure 1.7 reveal that carbon dioxide is a main factor in global warming and a preponderance of evidence shows that global warming will have adverse effects. As such, steps taken to reduce its concentration in the atmosphere can reasonably be assumed to combat further global warming. The efforts in Kyoto are just one example of efforts to reduce greenhouse emissions, specifically carbon dioxide. Because the generation of electricity

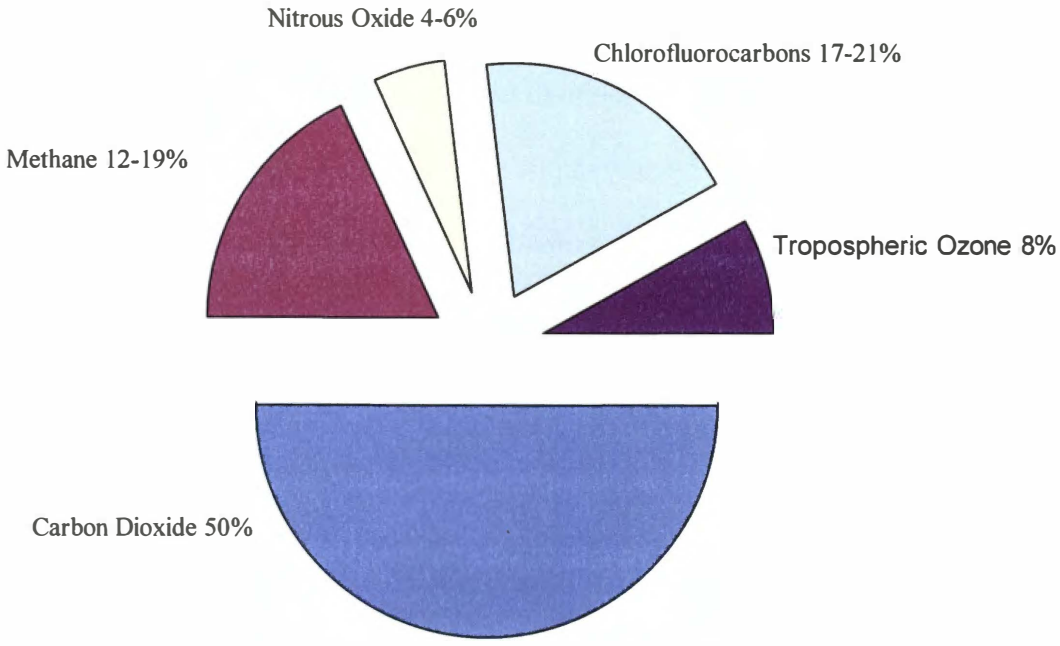

Figure 1.7. Estimated Greenhouse Gas Contributions to Global Warming

is the source of over one-third of the greenhouse emissions in the United States, it is a good place to focus efforts even more. This thesis will focus on one proposed solution for alleviating the environmental damage due to global warming—a semi-closed power generation cycle called the MATIANT cycle that uses fossil fuels but has the provision to exhaust no carbon dioxide to the environment.

Section 1.3. The Energy-Carbon Conflict. Table 1.1 in the previous section shows that world energy use will continue to increase, especially in developing nations. Accepting that the preferred method for producing that energy is the combustion of fossil fuels, the increases in carbon dioxide emissions shown in Table 1.2 are to be expected. Current scientific thought states that the long-term impacts of burning fossil fuels for

energy consumption are not compatible with maintaining the current global climate. However, as demand for energy, such as in the form of electricity, continues to increase, it seems likely that more fossil fuel will have to be burned to meet this demand. This is because the technology is already in place to use these fuels and because it exists in abundant supplies. According to a report by the United States Geological Survey [22], reserves for fossil fuels exist such that they can be used well into the future. The report says that natural gas supplies will last at least 44 years, oil for 60 years and coal for 300 years. The EIA [23] shows that, while coal comprises 56 percent of the fuel used by utilities to generate electricity, it emits 89 percent of the carbon dioxide associated with electricity production. While a familiar and available source of power, coal is clearly not environmentally friendly. This summarizes the quandary facing the power generating industry: an infrastructure already exists for continued use of abundant fossil fuel stores, but these fuels are environmentally damaging due to the copious amounts of greenhouse gases their combustion releases.

In order to implement any change in power generation, two criteria must be met for it to gain public approval. First, it must provide equal or greater benefits as the entrenched system. Second, there must not be an unreasonable cost increase associated with the change. A recent Time/CNN [24] poll supports these claims. The poll shows that 75 percent of the nation believes that global warming is a "fairly serious" to "very serious" problem and that 64 percent believes emissions of gases like carbon dioxide are causing global warming. However, the same poll reveals that less than half the nation would support tough government actions against global warming if utility bills went up or unemployment increased. While several solutions for reducing carbon dioxide

emissions have been set forth, projected increases show that there is still room for improvement. This section outlines some of the methods that may resolve this problem.

The most obvious answer to fight global warming is to stop carbon dioxide emissions altogether. While this would not immediately solve the problem due to the long atmospheric residence time of the greenhouse gas, it would be a definitive step in the right direction. The problem with this solution is that much of the world's energy and electricity come from sources that do emit carbon dioxide. Figure 1.2 provides visual evidence of this claim. Because of this, the result of ceasing the combustion of all fossil fuels would be a severe energy shortage. Therefore, science has sought ways to continue to use fossil fuels while reducing the carbon dioxide emissions to the atmosphere.

Section 1.4. Methods to Mitigate Carbon Dioxide Emissions. One solution is to increase the efficiency of fossil fuel burning systems. By doing this, the amount of fuel that must be burned to meet the world's energy needs is decreased, and consequently the amount of carbon dioxide emitted is also decreased. Strides have been made in this area. One measure of this is the energy intensity of a country. The energy intensity is the amount of energy required per unit of economic activity. From EIA [25] figures, the energy intensity of industrialized nations has been decreasing since 1970. While this is not the case for developing nations and EE/FSU, recent trends are beginning to show a decrease in the energy intensities for both and it is believed that this will continue and even accelerate into the twenty-first century. These results show that the world is becoming more efficient in its use of energy even as economies continue to grow.

In spite of these improvements in energy intensity, they are not enough. Table 1.1 and Table 1.2 both show that energy consumption and carbon dioxide emissions will

increase in the future. This is because the need for energy is increasing as the developing nations and EE/FSU strive to make their economies more like those of the industrialized nations. While the efficiency of energy production is increasing and therefore reducing per capita carbon dioxide emissions, this effect is cancelled out by the increasing demand for energy that produces an overall net gain in carbon dioxide emissions.

Fossil fuels are known as nonrenewable energy sources. They are not replenished at the same rate they are consumed. Another alternative to the problem of global warming is using renewable fuel sources such as wind, solar power, biomass, geothermal and hydropower. In addition to these, nuclear power, while also a nonrenewable energy source, can be used to generate power without carbon dioxide emissions. Both Figure 1.1 and Figure 1.2 reveal that these non-fossil fuel resources are used to produce appreciable, if not dominant, amounts of energy both in the United States and in the world.

While they are significant contributors to energy production, each of them also has some drawback. For instance, nuclear energy has the stigma that comes from catastrophic accidents and high costs due to strict regulations. Furthermore, the safe disposal of spent radioactive waste is the source of many disputes as well. It presents a problem that has yet to be solved. According to the Knoxville News-Sentinel [26], by the mid 1990s, only 103 of the original 131 nuclear plants in the United States were online, and 65 planned plants were cancelled. A report by the National Energy Policy Development Group [27] notes that the last completed nuclear energy plant in the United States was ordered in 1973. In spite of these facts, the EIA [28] notes that nuclear power is responsible for one-fifth of the electricity produced in the country. From EIA country reports [29], nuclear power is prominent in France, where it produces 38 percent of the

nation's electricity, and Sweden, where it produces 32 percent. However, there is still a great deal of public opposition for nuclear electricity to overcome.

Renewable resources often have storage or reliability problems. Wind power is dependent on wind velocity and the movement of air, which can be intermittent. The Wall Street Journal [30] reports the aesthetics of large windmill farms can be a problem and the windmill blades can be a danger to birds. Hydropower is dependent on a river, and the building of large dams to produce it can lead to problems like the flooding of farmlands or affect fish migration. Geothermal power requires underground hot springs or reservoirs and solar power comes from the sun, which is also an intermittent if predictable energy source.

Excluding hydropower, EIA [31] figures reveal that renewable energy sources account for less than 2 percent of the United States' energy consumption. The same is true in other industrial countries, but not in developing regions. The EIA [32] reports that 65 percent of Africa's energy comes from burning biomass such as wood. It is worth mentioning that the combustion of wood also creates carbon dioxide emissions. In addition to reliability problems, cost is also an issue for renewable power. The National Energy Policy Development Group [33], while noting the potential environmental advantages of renewable sources, also states that advanced technologies are needed and that the current high costs of some renewable resources such as solar must be reduced to make them competitive with power generation by fossil fuels. Renewable resources can best be characterized as part of the solution to reducing carbon dioxide emission, but not the sole answer. Table 1.3 on the following page shows the annual generation of

Table 1.3. Annual Electricity Generated by Renewable Resources in the United States

Renewable Resource	Annual Generation (10^6 kWh)
Solar	940
Wind	4460
Geothermal	13070
Biomass	36570
Hydropower	312000

electricity in the United States by renewable resources. As a point of comparison, the total annual generation of electricity in the United States is more than $3800*10^9$kWh [34].

If fossil fuels are to continue to be heavily used to generate power, then methods must be devised to lessen their impact on the environment, particularly their emission of greenhouse gases like carbon dioxide.

One such method of using fossil fuels in an environmentally friendly manner is fuel switching, which has already been exploited. This method involves switching the fuel for energy production from a fuel with a high carbon content to a fuel with a low carbon content. One example of this is switching from coal to natural gas. Table 1.4 on the following page from Smith [35], shows the carbon content in grams per MJ of some commonly used fuels.

As the table shows, there is an advantage to be gained by switching from coal to natural gas. This fact is further confirmed by the knowledge that while coal represents just over one half of the fuel used to produce electricity in the United States, it is responsible for almost 90 percent of the carbon dioxide emissions [36]. Therefore, any switch to natural gas from coal would mitigate carbon dioxide emissions. In fact, natural gas has been included in the electricity production of many countries, often in the form of

Table 1.4. Fuel Carbon Content

Fossil Fuel	CO_2 (grams of C/MJ)
Coal	25.1
Oil	20.8
Natural Gas	14.3
Peat	29.7
Wood	31.1

gas turbine/combined cycle power generation plants. However, coal is still readily available for use and estimates show that it will still exist in abundance long after natural gas resources have been depleted. Furthermore, even cutting carbon dioxide emissions in half will not solve the problem of greenhouse gas emissions.

Because coal exists in such large supply, it would behoove the world to find a way to use this resource in an environmentally friendly way. Coal is also attractive not only due to its low cost compared to other fossil fuels, as Figure 1.8 from the United States Department of Energy (USDOE) [37] shows, but also because of its abundance. This figure is displayed on the following page.

The USDOE [38] believes that it is possible to build a coal power plant that emits virtually no pollution at all. The Clean Coal Technology Program seeks to implement advanced technologies to reach the goal. Already, coal gasification plants have been built all over the world. In these plants, coal is converted to gaseous form, cleaned of its pollutants and then burned in a gas turbine. Beyond this, the program also is looking into converting coal to liquid methanol for use as a portable fuel. Electrochemical reactions from fuel cells are also a part of the program. Another benefit of advanced coal technology is the reduced energy required for carbon dioxide capture, as shown by

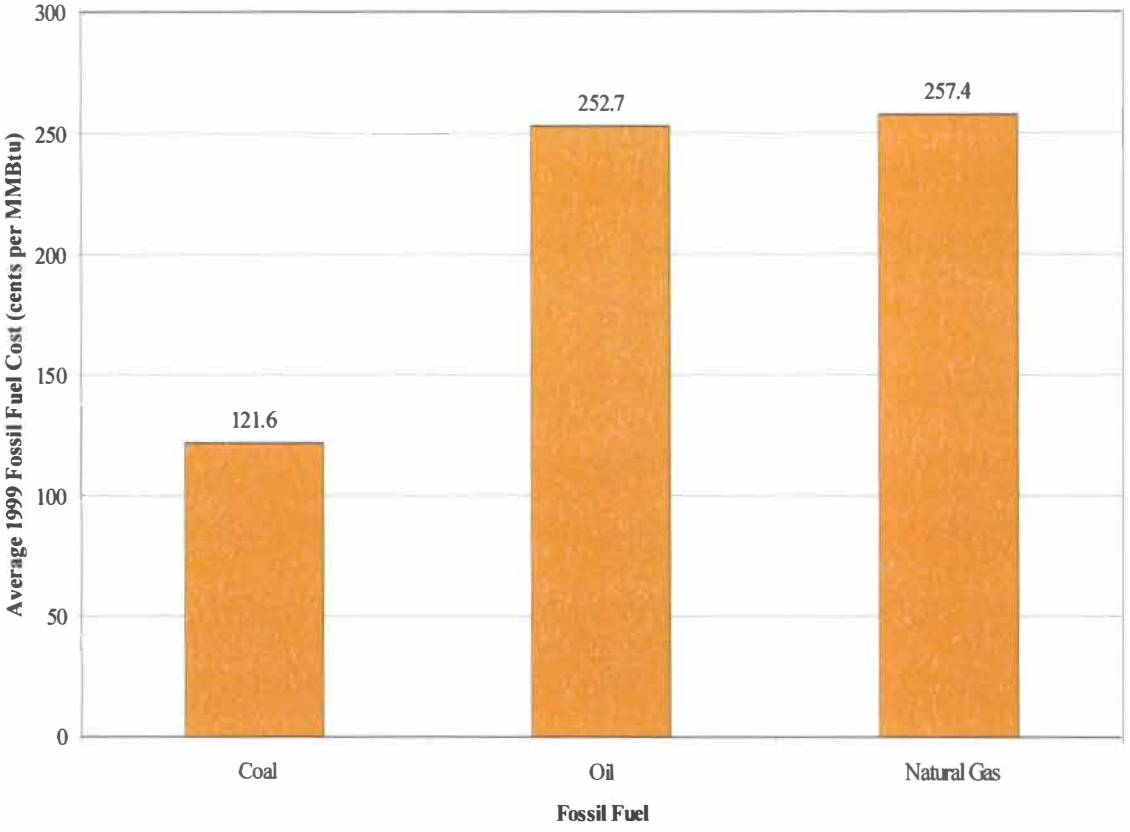

Figure 1.8. Comparison of Fossil Fuel Prices

Herzog [39]. For a 500 MW plant, as much as 100 MW may be required to capture carbon dioxide. Table 1.5 compares the energy penalty accompanying carbon dioxide capture for various types of power plants. Even though the primary goal of reducing carbon dioxide emissions is not economics or excess power, it can be seen in the table that not all methods of power generation using fossil fuels have high energy debits for removing carbon dioxide from the exhaust stream. This goes to show that efforts designed to combat global warming do not have to incur unreasonable costs and can even enhance performance.

Section 1.5. Sequestration of Carbon Dioxide. If carbon dioxide is to be produced, capturing and sequestering it rather than releasing it to the atmosphere could reduce its emission. Many different theories about the best method for carbon sequestration have been propounded. A USDOE [40] paper acknowledges that the goal of carbon sequestration is to keep anthropogenic carbon emissions from reaching the atmosphere by capturing, isolating and diverting them to secure storage. The President's Committee of Advisors on Science and Technology believes "A much larger science-based carbon dioxide sequestration program should be developed. The aim should be to provide a science-based assessment of the prospects and cost of carbon dioxide

Table 1.5. Carbon Dioxide Capture Energy Penalty

Type of Power Plant	Energy Penalty (%)
Conventional Coal	27-37
Gas	15-24
Advanced Coal	13-17

sequestration [41]." Another goal of the science is the removal of carbon dioxide from the atmosphere. The ocean is a natural sink for carbon dioxide, taking it up as a part of the natural carbon cycle. To promote this natural uptake, the USDOE [42] advances the idea of iron fertilization. As part of the Energy Laboratory at the Massachusetts Institute of Technology, the Carbon Sequestration Initiative studies various methods of storing carbon. The existence of such a project underscores not only the importance but also the potential for storing anthropogenic carbon. Several papers by Herzog explore the option of ocean sequestration of carbon dioxide. Herzog espouses several injection scenarios, including dry ice, dragging a pipe below a ship and building a platform with a pipe used to dispose of the compound [43]. Figure 1.9 gives a visual representation of several

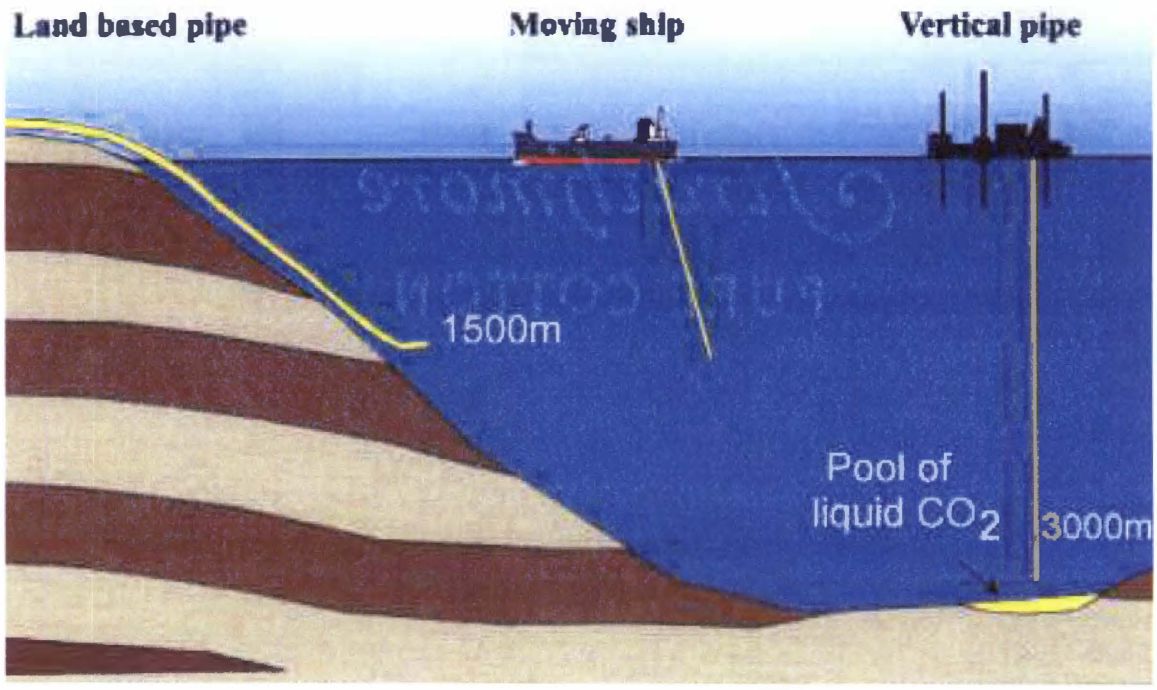

Figure 1.9. Various Methods to Introduce Carbon Dioxide for Ocean Storage

different ocean injection scenarios of carbon dioxide.

Herzog's group believes that release below 1000 meters (3280 feet) is best to ensure the desired residence time for the sequestered carbon dioxide [44]. Again, several difficulties accompany this method. In the ocean, carbon dioxide changes the pH of the water to be more acidic, which may adversely affect marine life [45]. Additionally, the technology to inject the carbon dioxide at the desired depth may be difficult to achieve. The dynamics of ocean currents may pose a problem and public perception may not support ocean storage of carbon dioxide. Herzog's group also states that depleted oil and gas wells, active oil wells and coal beds may be appropriate sequestration sites, but the integrity of the reservoirs must be determined before such a step is taken. Finding the best place to store the carbon dioxide is important because transportation costs figure heavily into the total cost for sequestration [46].

Bergman and Winter [47] write about disposing carbon dioxide in aquifers in the United States. They state that as much as 500,000 Megatons of carbon could be stored in these aquifers and that this option is attractive because 65 percent of the power generation plants in the United States are located near saline aquifers. In spite of their optimism the writers note that more work is need on the subject due to uncertainty about several limiting factors. Some concerns include leakage and actual useful storage volume, as well as local regulations or resistance to the injection.

Of particular interest is the carbon sequestration project done by Statoil, the Norwegian national oil company. The company strips the greenhouse gas from its production fields Sleipner East and West and injects it into aquifers 1000 meters (3280 feet) under the North Sea. In 1997, 660,000 tons of carbon dioxide were injected into

beds under the sea while the fields released 710,000 tons to the atmosphere. Thus, almost half of the total emissions of carbon dioxide were stored under the sea. According to the company, the International Energy Agency (IEA) states that the carbon dioxide emissions for the next 400 years from every European power plant could be stored under the North Sea [48].

The option of carbon sequestration is important because, given the right separation technique, fossil fuels can still be used to produce electricity while mitigating the emission of carbon dioxide. However, despite the early success of the Sleipner fields and the optimism of many scientists, a great number of technical and social issues are still present. A better grasp is needed of several issues before implementation of large-scale carbon dioxide sequestration. Prominent among these issues is the purity of the carbon dioxide to be sequestered, the soundness of the various storage media, the technology needed to accomplish the desired goal, the cost of the effort and public opinion. Nevertheless, based on the work done to date and current involvement in the project, capture and sequestration is a viable alternative that could play a large role in future generation of electricity.

Carbon dioxide sequestration figures prominently in the use of semi-closed cycles, which are described by Mathieu and Bolland [49]. A semi-closed cycle eliminates the need for scrubbers to capture carbon dioxide from flue gas but requires an air separation unit. The air separation unit produces pure oxygen, which is used to combust a fossil fuel, primarily natural gas. When this is done, the combustion products are carbon dioxide and water. The water can be easily separated by condensing it and separating the liquid from the carbon dioxide vapor, leaving only carbon dioxide to

circulate through the compressors and turbines. In this way, carbon dioxide is used to generate power. At an appropriate point in the cycle, a nearly 100 percent pure carbon dioxide stream can be separated and the rest re-circulated through the cycle. Thus, a semi-closed cycle is a regenerative gas cycle operating with carbon dioxide as the working fluid and using pure oxygen from an air separation unit in the combustion chamber(s). The separation of the carbon dioxide can be done mechanically rather than chemically because it is the only component present in the stream. The importance of sequestration can be easily seen, as the pure carbon dioxide stream is not freely exhausted to the atmosphere but can be sequestered in an appropriate storage medium. With modest extensions of current technology, semi-closed cycles can be constructed, thus making them available as valuable weapons in the arsenal against global warming in the intermediate term.

Section 1.6. The MATIANT Cycle. One example of a semi-closed cycle is the MATIANT cycle. Designed by Dr. Philippe MAThieu and Dr. Eugene IANTovsky [50], this cycle includes an air separation unit with a power generation plant. Figure 1.10 on the following page shows a process flow diagram of the MATIANT cycle.
Beginning at point *a*, a carbon dioxide and a trace amount water vapor enters a train of compressors with intercoolers. This serves to elevate the pressure of the carbon dioxide stream while the intercoolers cool the working fluid, lessening the work input such that the behavior of the compressor train approaches that of an Ericson cycle. The intercoolers also condense residual water vapor in the stream such that it can be removed from the process prior to separating some of the carbon dioxide for sequestration. The compressors are driven by turbines or motors (not shown) whose power can be drawn

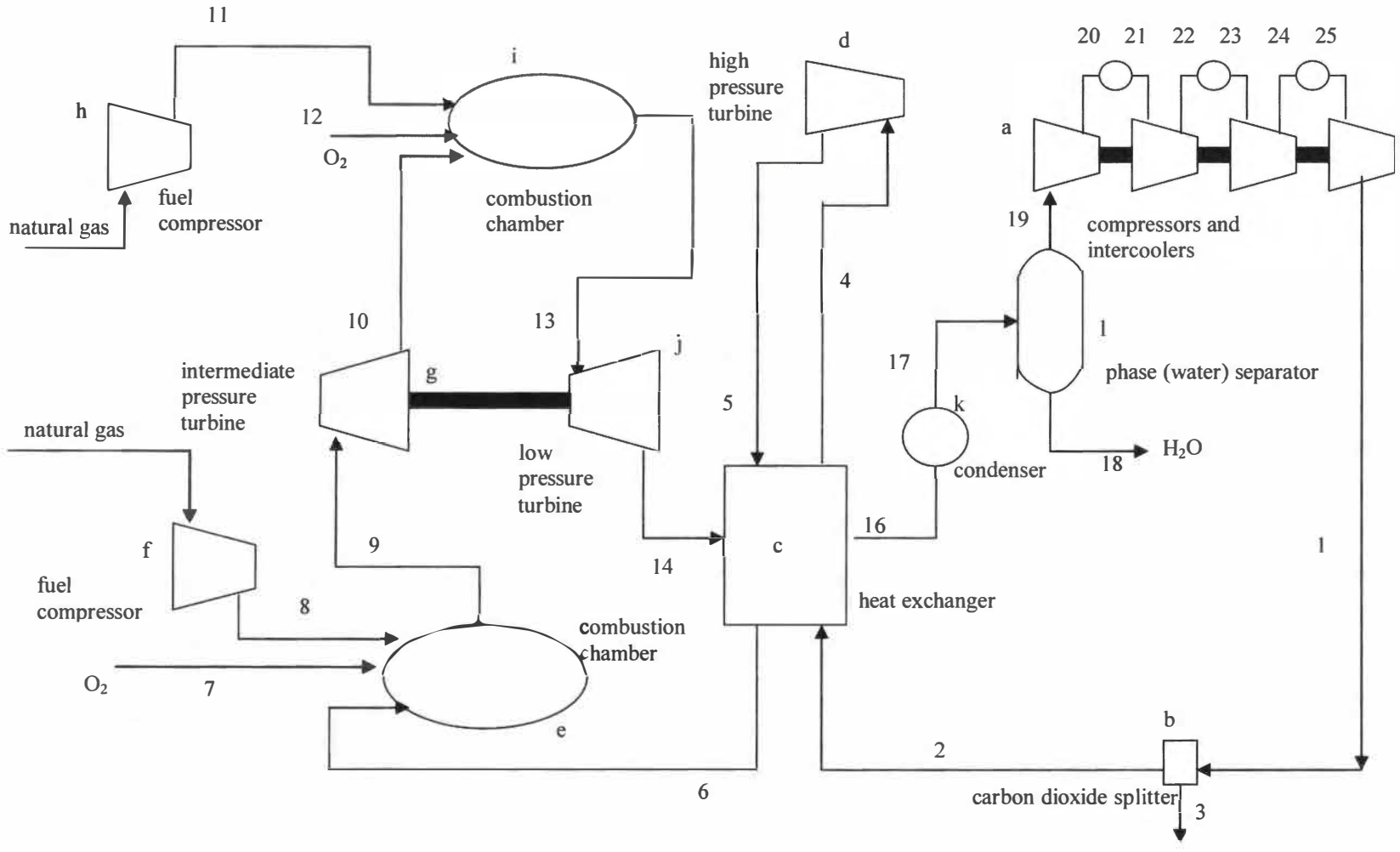

Figure 1.10. Process Flow Diagram of the MATIANT Cycle

either from that produced by the expanders in the cycle or from the power grid. After leaving the compressor train, the high-pressure carbon dioxide is split into two streams by splitter *b*. One stream can be sequestered by any combination of the methods listed above. The second stream is recycled for regenerative purposes. The stream enters heat exchanger *c* where it is heated and then proceeds to high-pressure expander *d*. Expander *d* is connected to a generator (not shown) that produces electricity from the expander work. The exiting stream is warmed in heat exchanger *c* and after leaving it enters combustion chamber *e*, which is also fed by oxygen from an air separation unit (not shown) and compressed natural gas that has been elevated to an appropriate pressure in natural gas compressor *f*, if necessary. The combustion products are carbon dioxide and water, both in the vapor phase. This mixture passes through an intermediate-pressure expander *g*, resulting in more work that a generator converts to electrical power. The carbon dioxide/water vapor passes into combustion chamber *i* where oxygen and natural gas that has been pressurized if necessary in natural gas compressor *h* are reacted. Again, the mixture exiting the combustion chamber is vaporized carbon dioxide and water. To balance the carbon dioxide withdrawn in splitter *b*, the correct amount of natural gas must be added to combustion chambers *e* and *i* and the stoichiometric amount of oxygen added to the combustion chambers as well. This ensures that the carbon dioxide stream is not depleted over time such that power production diminishes and that the amount of carbon dioxide does not increase such that the cycle cannot handle its load. Low pressure expander *j* again draws work from the stream. The stream passes through heat exchanger *c*, providing energy to heat the streams entering and exiting the high-pressure expander *d* as described earlier. This cools the carbon dioxide/water mixture, which is further cooled

in chiller *k*. When this is done, the most of water condenses while the carbon dioxide remains in gaseous form. To separate the liquid water from the gaseous carbon dioxide, separator *l* is employed. The resulting vapor stream is primarily carbon dioxide, with some residual water, which is then introduced into the compressor train to repeat the cycle described above.

In order to determine both the technical acceptability of this proposed solution, a proper analysis must be conducted. Ultimately, the project must not only be technically feasible, but must also be economically possible. However, before proceeding to a study of the economics of the project, it must be known whether or not it works and how its performance compares to that of an existing power plant that runs on natural gas. To achieve this end, this thesis will model and analyze the MATIANT cycle to determine if it meets both these criteria. The method to be employed in this endeavor is described in the next section.

Chapter 2. Modeling the MATIANT Cycle

Section 2.1. Software for Modeling the MATIANT Cycle. HYSYS software produced by Hyprotech is the software chosen to model the MATIANT cycle. At the time the thesis was commenced, this software was used by The University of Tennessee Chemical Engineering Department for process simulation. The availability of the software as well as the expertise on site at the university made it the logical choice to model the power plant.

HYSYS is a software that can be utilized to optimize new designs and improve existing process operations by means of process flowsheets. HYSYS can be used to ensure that optimal designs are identified and to model existing plants to ensure that equipment is meeting its performance specifications, evaluate retrofits and improve the overall process. HYSYS is also employed to rapidly screen alternative designs using efficient modeling and optimization techniques. The software allows engineers to incorporate steady state and dynamic modeling techniques to evaluate designs and rate existing plants. For the purposes of this project, the process flow diagram (PFD) and spreadsheet capabilities of HYSYS were used to build the MATIANT cycle model. In PFD mode, HYSYS allows for process flowsheets to be constructed graphically and then computes heat and material balances for the pieces of equipment or unit operations in the model. The spreadsheet function allows the user to manipulate simulation variables and perform custom calculations in the process flowsheet. The HYSYS spreadsheet supports complex mathematical formulas and Boolean logic in an interface, which is similar to conventional spreadsheets. Populating the spreadsheet with any variable is as easy as drag and drop. Calculations are performed simultaneously in the spreadsheet and the

PFD and can be done in both steady state and dynamic mode.

In each of the aforementioned modes, HYSYS uses colors and textboxes to inform the user what must be done to reach a converged process. A converged process is one in which the heat and material balances are fully calculated by HYSYS with no degrees of freedom remaining and, in the case of a cycle closed loops or recycle loops, the difference between the current and previous iteration is within a user defined tolerance. In the PFD mode, a unit operation that is red or yellow needs further definition, while streams that are light blue also need more inputs. Messages in the PFD mode also direct the user how to further define the active stream or piece of equipment so that it is fully defined. User inputs in the spreadsheet are shown in blue, while those properties calculated by HYSYS are black. The only variables that can be changed in the spreadsheet mode are those in blue. If a problem has been over constrained by the user, HYSYS will stop the calculation and give the user a message that identifies the where the calculation has been over defined.

Section 2.2. Constructing the MATIANT Cycle Model. Once a new model has been opened, the first step is to define what HYSYS calls a fluid package. This process entails defining an equation of state and the components that will make up the fluid streams in the model. For this thesis, a variation of the Peng-Robinson equation of state known as the PRSV equation of state is used. This equation of state is most commonly used in many HYSYS examples and is recommended in HYSYS user manuals. Discussions with HYSYS application engineers indicate a great deal of confidence in this equation of state due to extensive development work on it. Following the specification of the equation of state, the components of the streams must be identified. For the

MATIANT cycle, the components that will be present are methane (CH_4), oxygen (O_2), water (H_2O) and carbon dioxide (CO_2). Defining only these four components to be present in the MATIANT cycle implies that the fuel to be used is pure methane and that no other hydrocarbons are present in the fuel stream. Furthermore, the stream coming from the air separation unit is assumed to be pure oxygen. By not defining carbon monoxide to be part of the cycle, there is no provision for incomplete combustion of the fuel and oxidizer or for dissociation of the combustion products.

Once the equation of state and components of the streams have been defined, the PFD mode of HYSYS is entered and two streams are created. One of these streams is defined as having 100 percent CH_4 and the other stream is said to have 100 percent O_2. Each of these assumptions is a simplification. The fuel stream, while being predominantly CH_4, will have other hydrocarbons present in it such as ethane and propane and the stream from the air separation unit, which in practice is greater than 99 percent O_2, will contain trace amounts of inert gases such as nitrogen and argon. However, assuming 100 percent CH_4 and O_2 streams allows for the stoichiometric amounts of fuel and oxidizer to be easily determined and input into the model. It also eliminates the presence of inert compounds that would affect the reaction. Once the compositions of the fuel and oxidizer streams are determined, the temperature, pressure and flow rate of each stream is input. The fuel is assumed to be taken from an approximately 3500kPaa (508psia) pipeline at a temperature of 24°C (75°F) while the oxygen comes from an air separation unit and is input at the same pressure as the working fluid of the cycle at point 6 and a temperature of 140°C (284°F). The values that are entered in HYSYS are the English units: pounds per square inch and degrees Fahrenheit.

Although SI units are specified for modeling the MATIANT cycle, English units can be entered into the model. HYSYS allows for variables to be entered in any units and converts them to the defined SI unit set. For simplicity, the pressure of the oxygen is set at 3500psia and in the future the cycle pressure at this point (stream 6) will be set at 3500psia as well. The value of approximately 500psia for the pipeline pressure was determined from conversations with employees at Tengasco and the temperature is assumed to be the same temperature as ambient air. The flow rate of the oxidizer is defined by linking it to the flow rate of the fuel. As mentioned above, the compositions of the fuel and oxidizer are such that the stoichiometric ratio is easily known. The following equation sets this relationship: $CH_4+2O_2 \rightarrow CO_2+2H_2O$. Based on the above formula, two moles of oxygen react with one mole of methane to achieve one mole of carbon dioxide and two moles of water. This relationship can be used to set the molar flow rate of O_2 to be twice that of CH_4 so that the desired reaction occurs. HYSYS has a function called a "set block" that allows the user to set a variable of one stream using a defined variable for another stream. The set block contains both a multiplier and an offset. This logic is more fully described in a later section of this chapter. In the case of the O_2, the molar flow rate is set to be twice that of CH_4 with no offset. Streams 7 and 8 in Figure 1.10 are now fully defined.

The fuel and oxidizer streams are then input into a reactor that performs the reaction between CH_4 and O_2 that follows the above equation. In order to achieve a reaction between the fuel and oxidizer, a unit operation known in HYSYS as a Gibbs reactor is inserted. Normally, this reaction takes place in a combustion chamber. However, HYSYS is programmed such that all reactions take place in reactors. The

Gibbs reactor works so as to minimize the Gibbs free energy of a mixture, which in this case produces CO_2 and H_2O from the inputs of O_2 and CH_4. An optional input for the reactor is a heat stream that can be set to zero such that the reactor is assumed to be perfectly insulated or adiabatic; no heat from the reaction is lost to the surroundings. If no energy stream is input, HYSYS automatically assumes that the reactor is adiabatic. In this model, the stream is input and set equal to zero for thoroughness. Two streams exit the reactor: one liquid and one vapor. Due to the elevated temperature leaving the reactor, all the flow is vapor and HYSYS sets the flow rate of the liquid stream to be zero to recognize this fact. In spite of this, a liquid stream still must be inserted into the PFD in order to fully define the reactor. The streams are combined in a mixer such that a single stream moves on from reactor into the intermediate pressure turbine. Literature on the MATIANT cycle indicates the use of a maximum cycle temperature of 1300°C (2372°F) at the exit of the combustion chamber, so this value is input from the streams exiting the cycle. The pressure drop in the combustion chamber is assumed to be zero. When this is done, the reactor is fully defined and a fully defined vapor stream moves to the intermediate pressure turbine. This is stream 9 in Figure 1.10.

Stream 9 moves into the intermediate pressure turbine. For all turbines in the MATIANT cycle, the polytropic efficiency is set to be 85 percent. HYSYS allows for either the adiabatic or polytropic efficiency to be set for a turbine or compressor. Conversations with industry representatives indicate that polytropic efficiencies are normally used to define pieces of turbomachinery. A further reason for specifying the polytropic efficiency is provided by the Gas Process Suppliers Association. The polytropic process more closely represents the actual process of compression. An

isentropic process assumes that the compression is adiabatic. In practice, the heat of compression is not carried away during the process and the compression process behaves follows a polytropic curve [51]. Wilson defines the polytropic efficiency as the "small stage" efficiency because it serves to eliminate the influence of pressure ratio on the efficiency value for the piece of equipment [52]. In light of this, the polytropic efficiency is set at the above mentioned value. This value is consistent with both industry and academic experience. After setting the efficiency of the turbine, an outlet stream is connected to the intermediate pressure turbine. In Figure 1.10, this is stream 10. At this point, either the pressure or temperature of stream 10 can be set to fully define the turbine and its outlet stream. Since a pressure ratio is normally used to define a turbine, the pressure of the outlet stream is input by the user and HYSYS calculates the temperature and the turbine work. The composition and flow rate are already known because of the values input in stream 9. For a single inlet, single outlet unit operation, HYSYS automatically calculates the flow rate and composition without any action required by the user.

After the intermediate pressure turbine is another combustion chamber. Streams 11 and 12 are defined as the fuel and oxidizer, respectively. Stream 11 is defined in the same manner as stream 8, while stream 12 is set in the same way as stream 8. The only difference is the input pressure of the oxygen is set at the cycle pressure of 500kPaa (72.5psia). The fuel pressure is assumed to remain at 3500kPaa because expanding the CH_4 down to 500kPaa (72.5psia) would result in cryogenic temperatures in the process, necessitating the use of special materials and destroying energy and exergy or availability unnecessarily. The temperatures of streams 11 and 12 are the same as the corresponding

fuel and oxidizer streams entering the earlier combustion chamber. As before, a Gibbs reactor is modeled as the combustion chamber and is set to be adiabatic with an exit temperature 1300°C (2372°F). Additionally, a liquid stream must be defined and mixed with the vapor stream, but the elevated temperature ensures that all the flow is in the vapor phase. Stream 13 is the outlet stream that is now fully defined.

After exiting the second combustion chamber, the flow enters the low pressure turbine. As previously discussed, the only inputs that must be defined by the user are the polytropic efficiency of the turbine and the pressure of the stream exiting the low pressure turbine. The polytropic efficiency of the turbine is set at 85 percent and the outlet pressure is set at 115kPaa (16.7psia), slightly above atmospheric pressure. The pressure is kept above atmospheric because the stream still must pass through a heat exchanger and encounter a pressure drop prior to entering the compressor train. Setting the exit pressure from the low pressure turbine at this value ensures that the cycle pressure will remain above atmospheric pressure even though it will experience a further pressure decrease. HYSYS calculates the turbine work output and the temperature of the outlet stream. In this manner, stream 14 is defined.

The stream exiting the low pressure turbine is used to provide heating for the process stream that is exiting the high pressure turbine and to heat the process stream exiting the compressor train prior to its entrance to the high pressure turbine. This recovery of process heat is crucial to increasing cycle efficiency and ensuring that the energy input into the cycle from fuel is minimized. The actual MATIANT cycle will have one heat exchanger with three streams. However, this single heat exchanger is modeled as two heat exchangers. In one heat exchanger, stream 14 heats the stream

exiting the high pressure turbine, stream 5. In the second heat exchanger, stream 15, which is the cooled stream 14, heats stream 3, which is about to enter the high pressure turbine. The pressure drop through all heat exchangers is assumed to be two percent. The temperature of stream 15 is defined to be 700°C (1292°F). Literature on the MATIANT cycle indicates that the inlet temperature to the high pressure turbine is 675°C (1247°F). Consequently, the laws of heat transfer dictate that the inlet temperature of the hot stream be higher than the outlet temperature of the cold stream. A pinch point temperature of 25°C (45°F) is deemed appropriate for this application. The temperature of the exiting hot stream does not need to be defined, as the other three temperatures of the second heat exchanger are input by the user or program: the temperature exiting the compressor stream is set by HYSYS and the temperature of stream 4 the temperature of stream 15 are both input by the user. The pressure drop is again ensured to be two percent passing through the heat exchanger.

After passing through heat exchanger, the stream is a low pressure, low temperature vapor stream of carbon and water. Since the goal of the cycle is to sequester a pure carbon dioxide stream, the water must be removed from the cycle prior to splitting a stream for sequestration. This is primarily accomplished by cooling the stream in a condenser to near ambient temperature. Although the model constructed does not specify a cooling medium, ambient air or water is assumed to be capable of cooling the stream down to 30°C (86°F) and the pressure drop is again two percent. HYSYS calculates the amount of heat removed from the process. The cooling medium is not specified because it is not of importance in this technical analysis. Depending on the location of the MATIANT cycle, the cooling medium can be determined. Also, economics may play a

role in the decision, as the size, and thus the economics, of a heat exchanger depends on whether air, water or some other fluid is used to supply the required cooling. For the purposes of this model, it is enough that the working fluid is cooled down the required temperature. Stream 17 is now a two phase mixture of liquid water and mostly carbon dioxide vapor. The vapor phase contains a nominal amount of water that will be removed later. The two phase mixture enters a phase separator that splits the stream into two separate liquid and vapor streams. The liquid, stream 18, is a waste stream. On the other hand, the vapor stream, stream 19, enters the compressor train.

The compressor train is four stages of compression with three stages of intercooling. A journal article on the MATIANT cycle shows a maximum cycle pressure of 250 to 300 bara or 25000 to 30000kPaa (3626 to 4351psia) is acceptable. This model assumes a maximum cycle pressure of 256 bara or 25600kPaa (3713psia), or four stages of compression with a pressure ratio of approximately 4 in each stage. Stream 19 enters the compression train fully defined. Each compressor in the train is defined to have a polytropic efficiency of 80 percent per conversations with industry representatives. Once a compression stage has a defined polytropic efficiency, the outlet stage requires only a pressure or temperature to be fully defined. Because a compressor serves to produce a high pressure stream and it is known that a pressure ratio of approximately 4 is desired in each compressor, it is determined to input a pressure for the outlet stream. When this is done, HYSYS calculates the power required by the compressor stage and the temperature of the outlet stream, which is defined in Figure 1.10 as stream 20. Stream 20 enters an intercooler, where once again the cooling medium is not defined. A two percent pressure drop is applied to the stream going through the intercooler and the outlet temperature is

assumed to be 30°C (86°F). HYSYS determines the amount of heat removed from the stream and stream 21 exits the first intercooler fully defined. Some of the residual water in the working fluid is condensed at the elevated pressure and low temperatures present in the cycle after the intercooler, resulting in a two phase stream. This water is removed in a phase separator, with the liquid becoming a waste stream and the vapor stream continuing to the next stage of compression. This process just described repeats itself for two more stages. Following the third stage of compression, intercooling and phase separation there is a fourth page of compression that has the same inputs as the other three stages: polytropic efficiency and the pressure of the outlet stream. There is no intercooling following the fourth stage of compression. Stream 1 exits the fourth stage of compression as a mostly pure stream of carbon dioxide.

Stream 1 passes through a splitter where a percentage of the stream is split off from the main stream for sequestration. The method for determining the amount of working fluid split off will be discussed later in a section describing the cycle logic. Stream 2 is sent to sequestration while stream 3 is continues on in the cycle.

Stream 3 enters the heat exchanger and is heated by the exit stream from the low pressure turbine. The stream is warmed to add energy to it prior to expanding it in the high pressure turbine. This energy recovery increases the power that can be drawn from the high pressure turbine and also lowers the amount of cooling medium that must be used to reduce the temperature of the stream exiting the lower pressure turbine to ambient to condense a majority of the water in the cycle. Stream 3 experiences a two percent pressure drop in the heat exchanger and the exit temperature is defined at 675°C (1247°F) as mentioned earlier.

Stream 4 exits this heat exchanger and enters the high pressure turbine. Defining the turbine follows a method discussed twice before: the polytropic efficiency of the high pressure turbine is set at 85 percent and the pressure of outlet stream 5 is input as 3571kPaa (518psia). This pressure was chosen because it closely matches the pressure of the gas in the pipeline, per information provided by Tengasco. Some allowance is made in defining this pressure for pressure drop through the first heat exchanger. The temperature of stream 5 and the turbine power developed is found by HYSYS.

Stream 5 also passes through a heat exchanger, where it is warmed by the outlet stream from the low pressure turbine. The low pressure stream is simultaneously cooled by this process and a dual benefit is experienced: cycle energy is conserved and the low pressure stream is cooled as much as possible prior to ambient cooling to condense water. Stream 6 is a mostly pure carbon dioxide stream that enters the first combustion chamber along with stoichiometric amounts of pure CH_4 and O_2.

Because stream 6 is input into the first combustion chamber rather than being sequestered or becoming a waste stream, the cycle is a semi closed cycle rather than an open cycle. The cycle is semi closed because a portion of the stream exiting the compressor is sent to sequestration, while the rest remains in the cycle. A complete list of user defined variables in the HYSYS model can be found in an upcoming table.

Section 2.3. Logic in the MATIANT Cycle. The MATIANT cycle is determined for this project to be a net 250MW cycle with a maximum cycle temperature of 1300°C (2372°F). This temperature occurs after both combustion chambers in the process. In addition, a certain percentage of the stream exiting the compressor train will be split off and be sequestered. In order for the cycle to be steady state, the amount of

fluid removed from the cycle must be replaced by the fuel and oxidizer being input into the cycle. To ensure that certain cycle parameters are achieved, logic blocks in HYSYS are employed. Some of the logic blocks are necessary for cycle convergence, while others facilitate easier modeling of the process.

One such logic block is the set block. The set block has been discussed earlier in the chapter. A set block allows for a parameter in one stream to be defined using a parameter for another stream. The set block allows for the relationship to be a direct multiple or a direct multiple with an offset. This block is used to define the pressure drop across the intercoolers in the compressor train to be two percent and to set the molar flow rate of the oxygen from the air separation unit to be twice the molar flow rate of the fuel flow. Two set blocks control the oxygen flow rate, one for each combustion chamber in the MATIANT cycle. The set blocks make the molar flow rate of oxygen twice that of methane for each combustion chamber because this is the stoichiometric ratio. A set block is also used to set the molar flow rate of the carbon dioxide split out of the cycle for sequestration equal to the total molar flow rate of the fuel entering the cycle. This is because one mole of methane combusted in the stoichiometric amount of oxygen results in one mole of carbon dioxide. By doing this, the MATIANT cycle is made to be steady state. In total, six set blocks are present in the HYSYS model of the MATIANT cycle. None of them are needed to converge the cycle, but they decrease the amount of user manipulation required when the cycle parameters are varied. Table 2.1 on the following page shows the streams that are linked to other streams through set blocks in the model.

A logic block necessary to converge the HYSYS model is the recycle block. This block is needed because the MATIANT cycle is a loop. Calculation of the statepoints in

Table 2.1. Statepoints in MATIANT Cycle Model Defined Using SET Block

Set Variable	Linked to	Relationship	Comment
$\dot{n}_7$	$\dot{n}_8$	$\dot{n}_7 = 2 * \dot{n}_8$	Oxygen molar flow into first combustion chamber set to twice fuel (methane) molar flow
$\dot{n}_{12}$	$\dot{n}_{11}$	$\dot{n}_{12} = 2 * \dot{n}_{11}$	Oxygen molar flow into second combustion chamber set to twice fuel (methane) molar flow
P_{21}	P_{20}	$P_{21} = 0.98 * P_{20}$	Two percent pressure drop through first intercooler
P_{23}	P_{22}	$P_{23} = 0.98 * P_{22}$	Two percent pressure drop through second intercooler
P_{25}	P_{24}	$P_{25} = 0.98 * P_{24}$	Two percent pressure drop through third intercooler
$\dot{n}_2$	$\dot{n}_{11} + \dot{n}_8$	$\dot{n}_2 = \dot{n}_{11} + \dot{n}_8$	Molar flow of carbon dioxide split from main stream for sequestration is equal to molar flow of fuel input into process; ensures steady state process based on stoichiometric relationship

the cycle cannot proceed in a sequential manner because there is a recycle loop in the power plant. Thus, when a variable is changed, it cascades through the cycle and eventually returns to the point at which the change was made. To fully converge the cycle, an iterative process is required. From a practical standpoint, the inlet and outlet stream for the recycle block are the same stream. However, from a modeling standpoint, one stream is the values from the previous iteration while the other stream is the values HYSYS calculates for the stream after proceeding through the entire model. When the values from the previous iteration are compared to the new values and a predetermined tolerance is met, the cycle is considered converged. HYSYS allows for the user to set the tolerances to be different for the various properties. For example, a tolerance of 10°C

(18°F) may be desired for temperature, but because of the high flow rates, a tolerance of 100kgmol/hr can be set.

The third logic block used in HYSYS is the adjust block. Three such logic blocks are used in the MATIANT cycle model. When a certain value is desired for a stream, the adjust block can be used to ensure this value is met by adjusting the value of another statepoint that is input by the user. For example, if a temperature is required for a certain stream, then HYSYS can be told to adjust the flow rate or temperature of another stream to guarantee that the temperature requirement is met within a predetermined tolerance. Maximum and minimum bounds can be set on the variable being adjusted. Since the temperature of the outlet stream from each combustion chamber is to be 1300°C (2372°F), an adjust block is used in each instance. For the first combustion chamber, the temperature of stream 9 is set to 1300°C (2372°F) while the flow rate of stream 6 is adjusted so that this condition is met. The flow rate of stream 6 is important because it is used to cool the combustion products down to 1300°C (2372°F). Similarly, the temperature of stream 13 is set to 1300°C (2372°F) and the flow rate of stream 11, the fuel, is adjusted. The fuel stream must be chosen because the flow rate of stream 10 cannot be adjusted because it is not a user input into the process. A third adjust block is used to link the power output from the intermediate turbine to the flow rate of stream 8, the other fuel stream. This is because a net 250MW power plant is desired and the intermediate pressure turbine is the turbine that contributes the most power to the total gross turbine output. The power output for the intermediate pressure turbine is set at 205MW. Table 2.2 displays the relationship between adjusted variables and the values that the adjustments seek to ensure in the process.

Table 2.2. Statepoints in the MATIANT Cycle Defined Using the ADJUST Block

Target Variable		Adjusted Variable	Target Variable Tolerance	Comment
Stream	Setpoint			
T_9	1300°C (2372°F)	$\dot{n}_{11}$	±10°C (±18°C)	Exit temperature from first combustion chamber is set at 1300°C by adjusting molar flow of fuel stream
T_{13}	1300°C (2372°F)	$\dot{n}_6$	±10°C (±18°C)	Exit temperature from second combustion chamber is set at 1300°C by adjusting molar flow of inlet recycle stream
$\dot{W}_{ipturb}$	205MW	$\dot{n}_8$	5MW	Work output from intermediate pressure turbine, the largest power producing turbine in the cycle, is set at 205MW based by controlling fuel flow into first combustion chamber.

Because of the adjust and recycle blocks, there are certain variables that are input by the user into HYSYS that are changed by the program in an attempt to meet the constraints defined in the adjust block. For example, even though the user inputs a molar flow rate for stream 11, HYSYS will adjust this value in an effort to converge the cycle with a temperature of 1300°C (2372°F) for stream 13. Similarly, the outlet stream from the recycle block is continually changed by HYSYS as the cycle seeks to converge. The user inputs are updated as HYSYS goes through the various iterations to convergence. Because HYSYS changes certain statepoints in the process, there are fixed user inputs and variable user inputs. The values input by the user that are changed by HYSYS are

initial guesses in order to start the iterative process to achieve cycle convergence. Table 2.3, which displays all user inputs into HYSYS, distinguishes between fixed inputs and guesses in order to start the iterative process to achieve cycle convergence. The table does not include statepoints that are controlled by set or adjust blocks as depicted in Table 2.1 and Table 2.2, but it does include those inputs by the user that are changed by the adjust block to reach a target variable.

Section 2.4. HYSYS Output. Once the cycle is converged, a report can be printed from the worksheet portion of HYSYS. A large amount of information can be printed in these reports, including temperature, pressure, mass and molar flow rates, stream composition, mass and molar enthalpy, mass and molar entropy and more. Several different worksheets can be generated showing power terms, heat input or removal or compositions. The number of significant digits can be set by the user as can the order of the stream in the worksheet. If only certain streams are of interest, then the extraneous streams can be removed from the worksheet. HYSYS also denotes which values on the worksheet are input by the user. For the MATIANT cycle model, the power terms for the compressors and turbines are generated in report format as are the temperature, pressure, flow rate, enthalpy and entropy of the cycle streams.

Section 2.5. Modeling of the Simple Cycle. Part of this study involves the comparison of the MATIANT cycle to an air standard simple cycle power plant. Although a large number of power plants exist that could provide data for such a comparison, it is determined to construct a model in HYSYS of a simple cycle power plant. This will allow for cycle parameters to be set such that the simple cycle has many

Table 2.3. User Inputs into MATIANT Cycle Model

Input	Comment
P_1	Fixed
P_4	Fixed
T_4	Fixed
P_5	Fixed
P_6	Fixed
T_6	Variable
$\dot{n}_6$	Variable
P_7	Fixed
T_7	Fixed
P_8	Fixed
T_8	Fixed
$\dot{n}_8$	Variable
P_9	Fixed—no pressure drop assumed in first combustion chamber sets value
P_{10}	Fixed
P_{11}	Fixed
T_{11}	Fixed
$\dot{n}_{11}$	Variable
P_{12}	Fixed
T_{12}	Fixed
P_{13}	Fixed—no pressure drop assumed in second combustion chamber sets value
P_{14}	Fixed
P_{15}	Fixed—in HYSYS model but not in actual PFD due to heat exchanger modeling
T_{15}	Fixed
P_{16}	Fixed
P_{17}	Fixed
T_{17}	Fixed
P_{18}	Fixed—no pressure drop assumed in phase separator sets value
P_{19}	Fixed—no pressure drop assumed in phase separator sets value
P_{20}	Fixed
T_{21}	Fixed
P_{22}	Fixed
T_{23}	Fixed
P_{24}	Fixed

Table 2.3. Continued

Input	Comment
T_{25}	Fixed
ε_{poly} of low pressure expander	Fixed
ε_{poly} of intermediate pressure expander	Fixed
ε_{poly} of high pressure expander	Fixed
ε_{poly} of first compressor body	Fixed
ε_{poly} of second compressor body	Fixed
ε_{poly} of third compressor body	Fixed
ε_{poly} of fourth compressor body	Fixed
$COMPOSITION_6$	Variable
$COMPOSITION_7$	Fixed
$COMPOSITION_8$	Fixed
$COMPOSITION_{11}$	Fixed
$COMPOSITION_{12}$	Fixed
$\dot{Q}$ of first combustion chamber	Fixed—input only for thoroughness
$\dot{Q}$ of second combustion chamber	Fixed—input only for thoroughness

verification and to provide confirmation that the numbers that come out of the analysis of the MATIANT cycle are reasonable. Although the simple cycle constructed may not conform exactly to any existing plant, the efficiency and fuel use should still be similar to any other simple cycle plant.

To begin constructing the plant, it was determined that, like the MATIANT cycle, the power plant would not contain congeneration or be a combined cycle plant. Either one of these raises the efficiency of the plant and would not allow for an adequate comparison to be made. Furthermore, the simple cycle plant should have a similar net power output as the MATIANT cycle: 250MW. Like the MATIANT cycle, the simple cycle power plant has three stages of expansion and operates on natural gas. In addition, several statepoint inputs in the MATIANT cycle would be repeated in the simple cycle

model. Table 2.4 shows the parameters that are common between the two cycles. It should be noted that the maximum pressures of the MATIANT cycle and simple cycle are different. The maximum pressure in the MATIANT cycle is 25600kPaa (3713psia), while for the simple cycle the maximum pressure is 25100kPaa (3640psia). The exit stream from the compression train in the MATIANT cycle enters a heat exchanger, where it is warmed to the inlet temperature to the first expander. However, in the process of being warmed, the stream undergoes a two percent pressure drop to approximately 25100kPaa (3640psia). For the simple cycle, not such pressure drop is experienced. While the maximum cycle pressures are slightly different, the inlet pressure to the high pressure turbine is the same for each cycle, as Table 2.4 displays.

Figure 2.1 on the following page is a model of the simple cycle that is constructed in HYSYS. The following description of the process will refer to the statepoints and equipment noted in the figure.

Table 2.4. Statepoints with Similar Values in MATIANT Cycle and Simple Cycle Models

Statepoint	Value
Low Pressure Expander Inlet Temperature	1300°C
Intermediate Pressure Expander Inlet Temperature	1300°C
High Pressure Expander Inlet Temperature	675°C
Low Pressure Expander Inlet Pressure	500kPaa
Intermediate Pressure Expander Inlet Pressure	3500kPaa
High Pressure Expander Inlet Pressure	25100kPaa
Intercooler Outlet Temperature	30°C
Expander Polytropic Efficiency	85%
Compressor Polytropic Efficiency	80%
Net Work Output (approximate)	250MW
Gas Delivery Pressure	3500kPaa
Gas Delivery Temperature	24°C

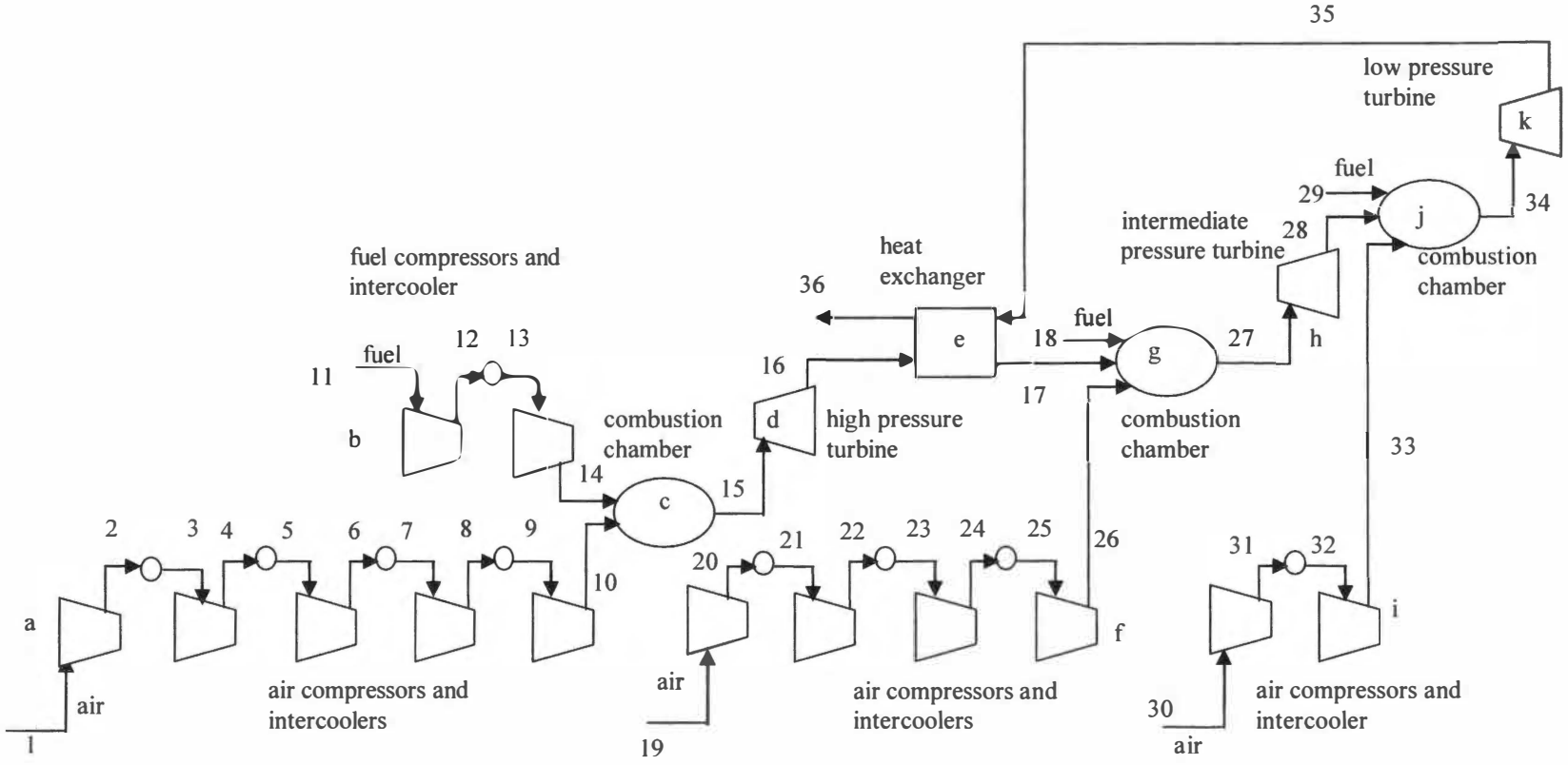

Figure 2.1. Schematic of Air Standard Simple Cycle Model

The process for modeling the simple cycle is like that described above for the MATIANT cycle model: the PRSV equation of state is used. The components of the cycle are then defined. The fuel for the simple cycle is the same as that for the MATIANT cycle: pure CH_4. The oxidizer is air, which is assumed for this analysis to be a two component mixture of 79 percent N_2 and 21 percent O_2. In addition, NO_2, CO_2 and H_2O are also defined to be constituents that are part of the fluid package. It is worth noting that defining a component to be included in the process does not mean that it will appear or has to appear. For example, NO_2 is defined because it is often included in the combustion products of a hydrocarbon fuel and air. However, it is normally present in only trace amounts. Whether or not it is observed in the combustion present in this cycle is dependent upon the calculations done by HYSYS.

To begin the model, the fuel and air streams are created. The fuel is at a pressure of 3500kPaa (508psia) as supplied by a pipeline and air is at ambient conditions: 1atm or 101.3kPaa (14.7psia) and 24°C (75°F). As is done for the MATIANT cycle, the English values are entered and HYSYS converts them to SI units. Because the simple cycle will have the same parameters as the MATIANT cycle at every possible point, the pressure at the inlet to the high pressure turbine is to be 25100kPaa (3640psia) in this model. Therefore, the air and fuel must both be compressed. The fuel is compressed in two stages with interstage cooling, *b*, while the air requires five stages with intercooling, noted as *a* in the figure. All compressor polytropic efficiencies are set at 80 percent, as is done in the MATIANT cycle base case. Also like the MATIANT cycle, the outlet temperatures from the air intercoolers are all 30°C (86°C). No cooling medium is defined for the intercoolers. For stream 1, atmospheric air, the composition, flow rate,

temperature and pressure are all needed to fully define the material stream. The same is true for stream 11, the fuel from the pipeline. Since the compressor polytropic efficiency is known, stream 2 and stream 12 need only to have their pressures defined. Stream 2 enters an intercooler where the temperature is reduced to the predetermined value, which is input by the user, and the pressure drops two percent, which is another use input. This defines stream 3. In a similar manner, streams 4, 6, 8 and 10 need only to have their pressures input, while streams 5, 7 and 9 require a pressure and a temperature input. The compression ratio is approximately 3.25 in each compressor, while each intercooler causes a two percent pressure drop and cools the working fluid down to 30°C (86°C). For the fuel, stream 12 enters an intercooler and stream 13 exits at 30°C (86°C) with a pressure two percent below that of stream 12. The pressure for stream 14 is entered to fully define it.

Once the fuel and air are compressed, they enter a combustion chamber, which is a Gibbs reactor as described for the MATIANT cycle. The Gibbs reactor has its optional energy stream set to equal zero to ensure that no heat is lost to the atmosphere. Although two exit streams must be specified in the HYSYS model, one liquid and one vapor, the temperatures are such that no liquid is present in the process. Because the temperature entering the high pressure turbine in the MATIANT cycle is 675°C (1247°C), the same temperature is desired to enter the high pressure turbine in the simple cycle. This is accomplished through an adjust block, which is linked to the molar flow rate of the air. Another adjust block is present to adjust the molar flow rate of the fuel such that complete combustion occurs in the Gibbs reactor: no methane will be present in the

combustion products. The pressure is set to remain constant through the combustion process. Stream 15 is now fully defined.

From the first Gibbs reactor, item *c* in Figure 2.1, the working fluid proceeds into a high pressure turbine, *d*, where the vapor is expanded to 3571kPaa (518psia) to produce work. The pressure of exit stream 16 is all that needs to be input for the stream to be fully defined, as the turbine polytropic efficiency is already known to be 85 percent. Stream 16 next enters a waste heat recovery unit, *e,* where reheat is provided by the exhaust from the low pressure turbine, which will be defined later. Stream 17 exits the heat exchanger, having undergone a two percent pressure drop to 3500kPaa (508psia) and been heated to 850°C (1562°F).

Stream 18 is defined to be pipeline fuel at the known conditions and stream 19 is atmospheric air. Stream 19 must undergo four stages of compression and intercooling in item *f* in Figure 2.1. There, streams 20, 22, 24 and 26 have their pressure input, while the pressure and temperature of streams 21, 23 and 25 are input. Thus all the aforementioned streams are fully defined. The exit temperature from all intercoolers is again 30°C (86°C) and a pressure drop of two percent occurs across all intercoolers. The pressure ratio in each stage of compression is approximately 2.45. Stream 18 does not need to be compressed before entering the second combustion chamber, *g*, along with streams 17 and 26.

The temperature for stream 27, which exits the second combustion chamber, is 1300°C (2372°F). This is the temperature at which the combustion products enter the intermediate turbine in the MATIANT cycle model. No pressure drop is assumed to take place in the perfectly insulated combustion chamber, which is also a Gibbs reactor. Two

adjust blocks are also used to ensure that the desired combustion temperature is achieved and that all the methane is consumed in the combustion process. The same variables are adjusted as for the first combustion chamber to arrive at these results.

Stream 27 expands through the intermediate pressure turbine, *h*, to 500kPaa (72.5psia). As the polytropic efficiency is set by the user as 85 percent, entering the pressure for stream 28 fully defines it. Stream 29 is next defined to be pipeline fuel and stream 30 is defined to be ambient air. The pipeline fuel goes into the third combustion chamber, while stream 30 is compressed in two stages of compression with intercooling, *i*, with a known polytropic efficiency of 80 percent. Each compressor in this train has a compression ratio of 2.25. The pressure of stream 31 is entered to fully define it, and it enters the intercooler and experiences a two percent pressure drop and is cooled to 30°C (86°F), which is input by the user to fully define stream 32. Stream 32 is compressed and stream 33 exits the compressor fully defined by the input of the user defined value of 500kPaa (72.5psia). Streams 28, 29 and 33 enter the third combustion chamber, *j,* which is an adiabatic Gibbs reactor with no pressure drop where the temperature is again increased to 1300°C (2372°F) to equal the temperature that enters the low pressure turbine in the MATIANT cycle. As is the case with the previous two combustion chambers, two adjust blocks are used, one to set the exit temperature and one to set the methane composition in the products to be zero. Stream 34 enters the last turbine stage, *k*, where it is expanded down to 115kPaa (16.7psia), the same pressure that exits the low pressure turbine in the MATIANT cycle. As with the previous two turbine stages, the polytropic efficiency of this stage is 85 percent. Stream 35 exits the turbine and is sent to heat exchanger *e* to provide some reheat to stream 16, the exhaust from the high pressure

turbine. The temperature of stream 36 as it exits the heat exchanger is calculated by HYSYS and pressure is input as 110kPaa (16.0psia). Stream 36 is then exhausted to the atmosphere, as the cycle is not designed to have cogeneration or to be a combined cycle.

Section 2.6. Logic in the Simple Cycle Model. No recycle block is needed in the simple cycle model, as it is not a closed loop cycle. The cycle statepoints can be calculated in a sequential manner and no iterative process is required to arrive at a fully converged cycle. Therefore, no recycle block is inserted in the model. Although set blocks could have been used to define pressure drops across the heat exchangers or combustion chambers, this is not done in the HYSYS model constructed. As discussed in the description of the model, six adjust blocks are employed in the model: three pairs that perform the same function around each of the Gibbs reactors in the cycle. One adjust block in each pair sets the exit temperature of the combustion chamber by adjusting the molar flow rate of air. The other adjust block sets the composition of the exhaust from the combustion chamber to contain no methane by controlling the molar flow of the fuel. This guarantees that complete combustion is modeled by HYSYS. A more complete description of the function and performance of adjust blocks can be found earlier in the chapter. Table 2.5 summarizes the adjusted variables and the target values used to ensure that the desired temperature and composition are achieved in the combustion products for the air standard simple cycle model.

Table 2.6 contains the user inputs into the simple cycle model and distinguishes whether they are fixed or variable inputs. The variable inputs are those that are changed by adjust blocks to arrive at a target value for a certain statepoint. The target values set in the adjust blocks are not contained in Table 2.6.

Table 2.5. Statepoints in the Air Standard Simple Cycle Defined Using the ADJUST Block

Target Variable		Adjusted Variable	Target Variable Tolerance	Comment
Stream	Setpoint			
T_{15}	675°C	$\dot{n}_1$	±10°C	Exit temperature from first combustion chamber is set at 675°C by adjusting molar flow of the oxidizer stream
$COMPOSITION_{15}$	CH_4=0	$\dot{n}_{11}$	±0.1%	Methane content in exit stream from first combustion chamber is set to zero by ajusting molar flow of inlet fuel stream—this is modeling of complete combustion
T_{27}	1300°C	$\dot{n}_{19}$	±10°C	Exit temperature from second combustion chamber is set at 1300°C by adjusting molar flow of the oxidizer stream
$COMPOSITION_{27}$	CH_4=0	$\dot{n}_{18}$	±0.1%	Methane content in exit stream from second combustion chamber is set to zero by adjusting molar flow of inlet fuel stream—this is modeling of complete combustion
T_{34}	1300°C	$\dot{n}_{30}$	±10°C	Exit temperature from third combustion chamber is set at 1300°C by adjusting molar flow of the oxidizer stream
$COMPOSITION_{34}$	CH_4=0	$\dot{n}_{29}$	±0.1%	Methane content in exit stream from third combustion chamber is set to zero by ajusting molar flow of inlet fuel stream—this is modeling of complete combustion

Table 2.6. User Inputs into Simple Cycle Model

Input	Comment
P_1	Fixed
T_1	Fixed
$\dot{n}_1$	Variable
P_2	Fixed
P_3	Fixed
T_3	Fixed
P_4	Fixed
P_5	Fixed
T_5	Fixed
P_6	Fixed
P_7	Fixed
T_7	Fixed
P_8	Fixed
P_9	Fixed
T_9	Fixed
P_{10}	Fixed
P_{11}	Fixed
T_{11}	Fixed
$\dot{n}_{11}$	Variable
P_{12}	Fixed
P_{13}	Fixed
T_{13}	Fixed
P_{14}	Fixed
P_{15}	Fixed—no pressure drop assumed in first combustion chamber sets value
P_{16}	Fixed
P_{17}	Fixed
T_{17}	Fixed
P_{18}	Fixed
T_{18}	Fixed
$\dot{n}_{18}$	Variable
P_{19}	Fixed
T_{19}	Fixed
$\dot{n}_{19}$	Variable
P_{20}	Fixed
P_{21}	Fixed
T_{21}	Fixed
P_{22}	Fixed

Table 2.6. Contined

Input	Comment
P_{23}	Fixed
T_{23}	Fixed
P_{24}	Fixed
P_{25}	Fixed
T_{25}	Fixed
P_{26}	Fixed
P_{27}	Fixed—no pressure drop assumed in second combustion chamber sets value
P_{28}	Fixed
P_{29}	Fixed
T_{29}	Fixed
$\dot{n}_{29}$	Variable
P_{30}	Fixed
T_{30}	Fixed
$\dot{n}_{30}$	Variable
P_{31}	Fixed
P_{32}	Fixed
T_{32}	Fixed
P_{33}	Fixed
P_{34}	Fixed—no pressure drop assumed in third combustion chamber sets value
P_{35}	Fixed
P_{36}	Fixed
ε_{poly} of low pressure expander	Fixed
ε_{poly} of intermediate pressure expander	Fixed
ε_{poly} of high pressure expander	Fixed
ε_{poly} of first air compressor body	Fixed
ε_{poly} of second air compressor body	Fixed
ε_{poly} of third air compressor body	Fixed
ε_{poly} of fourth air compressor body	Fixed
ε_{poly} of fifth air compressor body	Fixed
ε_{poly} of sixth air compressor body	Fixed
ε_{poly} of seventh air compressor body	Fixed
ε_{poly} of eighth air compressor body	Fixed
ε_{poly} of ninth air compressor body	Fixed

Table 2.6. Continued

Input	Comment
ε_{poly} of tenth air compressor body	Fixed
ε_{poly} of eleventh air compressor body	Fixed
ε_{poly} of first fuel compressor body	Fixed
ε_{poly} of second fuel compressor body	Fixed
$COMPOSITION_1$	Fixed
$COMPOSITION_{11}$	Fixed
$COMPOSITION_{18}$	Fixed
$COMPOSITION_{19}$	Fixed
$COMPOSITION_{29}$	Fixed
$COMPOSITION_{30}$	Fixed
$\dot{Q}$ of first combustion chamber	Fixed—input only for thoroughness
$\dot{Q}$ of second combustion chamber	Fixed—input only for thoroughness

Chapter 3. Methodology for a Thermodynamic Evaluation of the MATIANT Cycle

Section 3.1. Motivation for Analysis. Due to a well established infrastructure based on the use fossil fuels to generate power and the development of technologies to support this method, any new power generation concept should make use of these assets while eliminating the problems inherent to them. In particular, the emission of carbon dioxide and nitrous oxides associated with the combustion of fossil fuels with air has become a major concern of the world community. As has been shown in earlier chapters, the MATIANT power cycle is proposed to meet both of these demands. To take the MATIANT cycle from concept to reality, its technical feasibility must be established. This thesis provides a comparison between a natural gas fired power plant cycle and the MATIANT power plant cycle to determine if the MATIANT cycle is indeed a potential method for generating power. In addition, the components and certain vital statepoint values of the MATIANT cycle are analyzed in order to ascertain a better idea of the plant's performance and ways that it can be enhanced.

Section 3.2. Comparison to a Simple Cycle Power Plant. The performance of the MATIANT cycle compared to an air standard simple cycle power plant is a key factor in determining the feasibility of constructing the proposed power plant. If the MATIANT cycle does not compare favorably to a traditional air standard simple cycle power plant on a technical level, then its acceptance is not likely. HYSYS is used to construct and analyze a simple cycle power plant, shown in Figure 2.1, where the fuel is natural gas and the oxidizer is air. Like the MATIANT cycle under consideration in Figure 1.10, the simple cycle will not have any cogeneration or combined cycle capability. The simple

cycle power plant model is set up to ensure that the main cycle parameters are the same as those of the proposed MATIANT cycle. Both the MATIANT cycle and the simple cycle plant will have three stages of expansion. Although the design MATIANT cycle is a departure from an air standard power plant, setting key performance parameters to be equal allows for a standardized comparison to be made between a conventional power plant and a proposed "next generation" power plant.

To realize this goal, the inlet temperature to each turbine in the simple cycle model is the same as that found in the MATIANT cycle model. Similarly, the pressure of the working fluid entering and exiting each expander stage is the same in the simple cycle as in the MATIANT cycle. For all turbomachinery, the polytropic efficiencies are the same: turbines in both power plants have a polytropic efficiency of 85 percent while compressors have a polytropic efficiency of 80 percent. The various compression trains in the simple cycle employ intercooling to lower the stream temperature to 30°C (86°F), the same as that found in the base case of the MATIANT cycle. Further discussion on the modeling of the simple cycle can be found in the "Modeling" chapter of this report. Table 3.1, repeated from the "Modeling" chapter, shows the inputs into the simple cycle model that are the same as those of the MATIANT cycle model.

The simple cycle and the MATIANT cycle will be compared using the first and second law efficiency and the fuel usage of each plant. These numbers provide quick insight into the relative performance of each plant. The first law efficiency makes use of the first law of thermodynamics, the conservation of energy, to calculate the efficiency of a process. In words, the first law of thermodynamics states that the time rate of change of energy in a control volume is equal to the difference in the energy entering the control

Table 3.1. Statepoints with Similar Values in MATIANT Cycle and Simple Cycle

Statepoint	Value
Low Pressure Expander Inlet Temperature	1300°C
Intermediate Pressure Expander Inlet Temperature	1300°C
High Pressure Expander Inlet Temperature	675°C
Low Pressure Expander Inlet Pressure	500kPaa
Intermediate Pressure Expander Inlet Pressure	3500kPaa
High Pressure Expander Inlet Pressure	25100kPaa
Intercooler Outlet Temperature	30°C
Expander Polytropic Efficiency	85%
Compressor Polytropic Efficiency	80%
Net Work Output (approximate)	250MW
Gas Delivery Pressure	3500kPaa
Gas Delivery Temperature	24°C

volume by heat transfer per unit of time and leaving the control volume by work per unit if time. By this convention, heat transfer per unit time to the control volume is considered positive and heat transfer from the control volume is considered negative. Furthermore, the work per unit time done by the control volume is positive, while the net work per unit time performed on the control volume is negative. Equation 3.1 from Moran and Shapiro [53] summarizes the law.

$$\frac{dE}{dt} = \dot{Q} - \dot{W} + \sum_{i}^{N_I} \dot{n}_i \cdot \left(h_i + \frac{V_i^2}{2} + g \cdot z_i \right) - \sum_{e}^{N_E} \dot{n}_e \cdot \left(h_e + \frac{V_e^2}{2} + g \cdot z_e \right) \qquad (3.1)$$

In the case of the MATIANT cycle analysis, steady state is assumed, so $\frac{dE}{dt} = 0$.

Furthermore, potential and kinetic energy effects are assumed to be negligible such that $\sum_{i}^{N_I} \dot{n}_i \cdot \left(\frac{V_i^2}{2} \right) - \sum_{e}^{N_E} \dot{n}_e \cdot \left(\frac{V_e^2}{2} \right) = 0$ and $\sum_{i}^{N_I} \dot{n}_i \cdot (g \cdot z_i) - \sum_{e}^{N_E} \dot{n}_e \cdot (g \cdot z_e) = 0$. With these

constraints, the conservation of energy equation for a control volume becomes what is shown in equation 3.2.

$$\dot{Q} + \sum_{i}^{N_I} \dot{n}_i \cdot h_i = \dot{W} + \sum_{e}^{N_E} \dot{n}_e \cdot h_e \tag{3.2}$$

The first law, or thermal, efficiency of a cycle based on the higher heating value of the fuel is shown in equation 3.3 provided by Moran and Shapiro [54].

$$\varepsilon_{HHV} = \frac{\dot{W}_{net}}{\dot{Q}} \cdot 100 \tag{3.3}$$

The equation states that the efficiency of the cycle is the ratio of the net power output of the cycle, $\dot{W}_{net}$, and the net amount of heat input into the cycle by combustion, $\dot{Q}$. For this investigation, the value $\dot{Q}$ is found by multiplying the higher heating value of the fuel by the total fuel flow rate.

$$\dot{Q} = \dot{n}_{fuel} \cdot HHV_{fuel} \tag{3.4}$$

On the basis of the amount of energy added to a cycle, it can be determined from this equation what percentage of the total energy added to a system is recovered as a product, in this case power. The higher heating value is defined by Moran and Shapiro as the amount of heat released by the combustion of one mole of fuel in air, assuming that all the water in the products is in the liquid phase [55]. The higher heating value is greater than the lower heating value because it does not take into account the latent energy required to vaporize the liquid water in the combustion products. These values are well known and tabulated for many different fuels.

The second law efficiency of the cycle is found using the second law of thermodynamics, which says that the rate of entropy change in a control volume is equal

to the sum of the rate of entropy transfer accompanying heat transfer per unit time, net entropy inflow to a system per unit of time and entropy production per unit of time. The following formula from Moran and Shapiro [56], shown in equation 3.5, displays this relationship.

$$\frac{dS}{dt} = \sum_{j}^{N_Q} \frac{\dot{Q}_j}{T_j} + \sum_{i}^{N_I} \dot{n}_i \cdot s_i - \sum_{e}^{N_E} \dot{n}_e \cdot s_e + \dot{\sigma} \tag{3.5}$$

Due to the steady state assumption, $\frac{dS}{dt} = 0$, the second law for a control volume simplifies to equation 3.6.

$$\sum_{j}^{N_Q} \frac{\dot{Q}_j}{T_j} + \sum_{i}^{N_I} \dot{n}_i \cdot s_i - \sum_{e}^{N_E} \dot{n}_e \cdot s_e + \dot{\sigma} = 0 \tag{3.6}$$

Multiplying the steady state equation for the second law, equation 3.6, by T_o and then subtracting the resulting equation from equation 3.2 leads to an equation for the availability flowing into and out of a control volume. Availability is defined by Moran and Shapiro as the maximum useful work that can be obtained as two systems interact to equilibrium. One of the systems is the environment, which has a uniform temperature and pressure. When the other system is in equilibrium with the environment, it is said to be in the dead state [57]. The dead state for this thesis is determined to be 1atma or 101.3kPaa (14.7psia) and 25°C (77°F). Utilizing the aforementioned assumptions, the change in the flow availability or time rate of availability change of a steady state system, neglecting potential and kinetic energy effects, is given by Moran and Shapiro [58] and shown in equation 3.7.

$$\begin{aligned}
&\psi_2 - \psi_1 \\
&= \sum_{i}^{N_I} \dot{n}_i \cdot (h_i - T_o s_i) - \sum_{e}^{N_E} \dot{n}_e \cdot (h_e - T_o \cdot s_e) \\
&= \dot{W} - \sum_{j} \dot{Q}_j \cdot \left(1 - \frac{T_o}{T_j}\right) + \dot{I}
\end{aligned} \tag{3.7}$$

In equation 3.7, $\dot{I} = T_o \cdot \dot{\sigma}$ defines the irreversibility or "lost work" of the process [59]. The flow availability of a given stream, ignoring changes in kinetic and potential energy, is shown in equation 3.8 as given by Moran and Shapiro [60].

$$\psi = \sum_{e}^{N_E} \dot{n}_e \cdot (h_e - h_o - T_o \cdot (s_e - s_o)) \tag{3.8}$$

The second law, or exergetic, efficiency of a cycle is defined as the ratio of the net power output, $\dot{W}_{net}$, to the rate of total availability added, ψ_{total}, in the combustion process. Therefore, $\psi_{total} = \psi_{products} - \psi_{reactants}$. Any stream that enters the combustion chamber, including any inert components, are contained in the $\psi_{reactants}$ term. The availability contribution from each individual combustion process is summed up to arrive at the total availability added to the working fluid. Equation 3.9 shows the formula that represents this relationship.

$$\eta = \frac{\dot{W}_{net}}{\psi_{total}} \cdot 100 \tag{3.9}$$

This equation differs from the first law efficiency in that the result calculates how much of the useful energy input into the cycle is seen as a power output. The first law efficiency makes no such allowance for useful energy. Thus, the second law efficiency is typically higher than the first law efficiency. This is true because the value in the

denominator of the second law efficiency equation, ψ_{total}, is smaller than the value in the denominator of the first law efficiency equation, $\dot{Q}$. The useful energy in a stream, or the availability, is less than or equal to the total energy contained in the stream, but never exceeds the value of the total energy input to a process.

The fuel usage for the two power plants can be easily obtained from the HYSYS output reports. Fuel usage is a consideration in operating expenses of a power plant and will provide another measuring stick for how the MATIANT cycle compares to a standard cycle. Another measure of the fuel usage of a power plant is the heat rate. The heat rate is a measure of how much energy from the fuel is required to produce a certain amount of energy output from the plant. The units of heat rate are kJ/kWh. The calculation to find the heat rate for the MATIANT cycle and the simple cycle is shown in equation 3.10.

$$\alpha = \frac{HHV_{fuel} \cdot \dot{n}_{fuel}}{\dot{W}_{net}} \tag{3.10}$$

A higher heat rate portends a less efficient process.

Section 3.3. Individual Component Performance. Analyzing the individual component performance of the MATIANT cycle will serve to provide a more in depth look at the process to determine the sources of greatest inefficiency or irreversibility. This will increase the overall understanding of the cycle and provide some direction as to where future efforts should be focused to improve the cycle's performance. This investigation will be based on a second law analysis and will show how much useful work is destroyed or lost in each component. The MATIANT cycle has nineteen total

components, which can be grouped into five categories. For all components, it is assumed that they are adiabatic and thus lose no heat to the atmosphere. The analyses below are a summary of material found in Moran and Shapiro [62].

One such category is the compressor, a typical diagram of which is shown below in Figure 3.1. No sidestreams are shown, as none are contained in the MATIANT cycle.

A compressor serves to increase the pressure, and consequently the temperature, of a vapor. Due to inefficiency and irreversibility, more power must be put into a compressor than is actually needed to compress the fluid to its desired pressure. The second law efficiency of a compressor is the ratio of the availability added to the fluid to the power required by the compressor. This relationship is shown in equation 3.11.

$$\eta = \frac{\Psi_2 - \Psi_1}{\dot{W}_{comp}} \cdot 100 \tag{3.11}$$

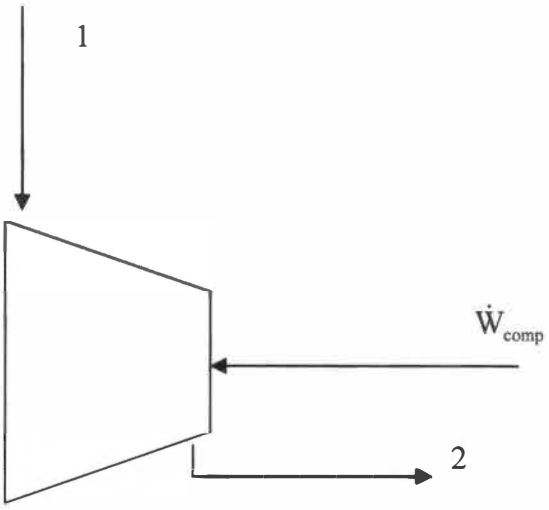

Figure 3.1. Compressor Schematic

The equation for the irreversibility produced by compression is displayed in equation 3.12.

$$\dot{I} = \dot{n} \cdot T_o \cdot (s_2 - s_1) \tag{3.12}$$

Another category of equipment in the MATIANT cycle is the turbine. Figure 3.2 is a sketch of an expansion process common to many power plants. Like the compressor drawing in Figure 3.1 above, this expander is a single inlet, single outlet component like those found in the MATIANT cycle.

The purpose of a turbine is to expand a high pressure, high temperature vapor, producing work in the process. A turbine produces less work than anticipated for a given expansion due to irreversibility. As can be depicted in equation 3.13, the second law efficiency of a turbine is the ratio of the actual work produced by the turbine and the availability change in the fluid passing through the turbine.

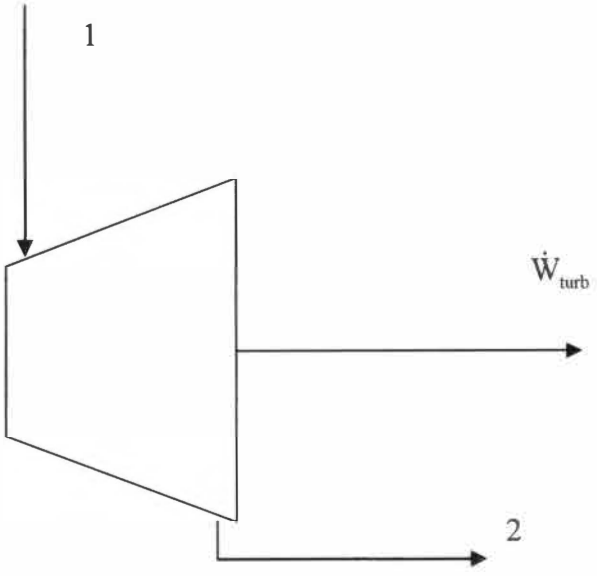

Figure 3.2. Turbine Diagram

$$\eta = \frac{\dot{W}_{turb}}{\psi_1 - \psi_2} \cdot 100 \tag{3.13}$$

The equation for calculating the irreversibility produced by the expansion process is shown below in equation 3.14.

$$\dot{I} = \dot{n} \cdot T_o \cdot (s_2 - s_1) \tag{3.14}$$

Several heat exchangers are present in the MATIANT cycle. Some of these are required to cool the working fluid, such as the intercoolers and condenser, while the central heat exchanger cools the process fluid for one portion of the cycle while providing heat for another stream in the cycle. Figure 3.3 provides a schematic of a cross flow, two-channel heat exchanger, similar to what is required for most applications in the MATIANT cycle. In the figure, it can be assumed that stream 1 is the incoming warm stream, while stream 3 is the incoming cold stream.

The procedure to determine the irreversibility and inefficiency of a heat exchanger depends on whether the heat exchanger is present to provide cooling or heating to a given stream. For the intercoolers and the condenser, it can be assumed that their purpose in the cycle is to cool the working fluid. The working fluid is above the

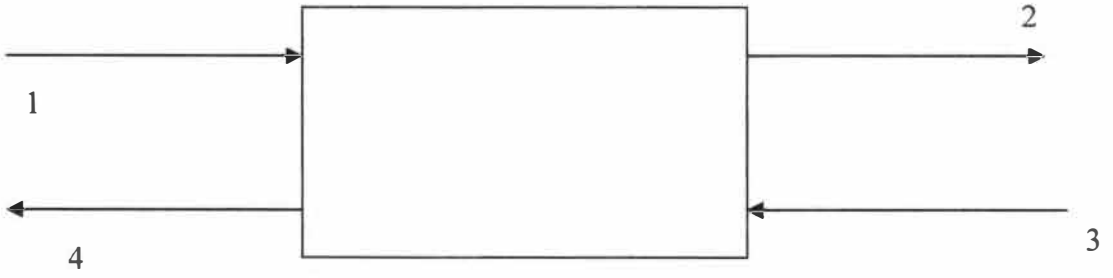

Figure 3.3. Two-Channel Cross Flow Heat Exchanger

dead state, meaning that cooling this fluid will bring is closer to the dead state; that is, the flow availability of the stream is decreased. The intercoolers and condenser are present in the cycle to provide cooling to hot streams in order to lower the compression power. The stream that provides the cooling is not a part of the cycle; it is a waste stream that cools the working fluid and then exits the process. The availability transferred to this stream is therefore not reused in the cycle. Therefore, the efficiency of the heat exchanger is not important from a thermodynamic standpoint. When economics and facility design are considered, the efficiency of the heat exchanger is important because it affects the size of the component and therefore its cost. However, from the view of accounting for all availability destroyed in the process, it is important to calculate the irreversibility of the intercoolers and condenser. In the modeling of the MATIANT cycle in HYSYS, no cooling stream is shown for the intercoolers and the condenser; the process flow diagram shows an energy stream being removed from the cycle. The equation that shows the irreversibility associated with the cooling of the process stream is shown in equation 3.15.

$$\dot{I} = \dot{n} \cdot T_o \cdot (s_1 - s_2) \tag{3.15}$$

Normally, such an equation would contain the availability added to the cool streams. However, since in the model these are waste streams, the availability added to these streams is of no interest in this study. Furthermore, the MATIANT cycle that is modeled does not contain a specific cooling stream, as this will depend on the location of the plant and many other factors. For this reason, the calculation of the irreversibility generated in the condenser and intercoolers is limited to the working fluid. This point is discussed in more detail in the Modeling chapter of this thesis.

In the case of the central heat exchanger in the process, which warms the fluid exiting the compressor before it enters the high pressure turbine and then warms the exhaust stream from the high pressure turbine, all to provide reheat or to add availability to the process stream by using an exhaust stream from another part of the cycle, it can be presumed that the heat exchanger's purpose is to provide heat to a process stream. This heat exchanger is a three channel heat exchanger rather than a two channel heat exchanger as shown in Figure 3.3 above. Figure 3.4 below depicts a schematic of the central heat exchanger in the MATIANT cycle. In Figure 3.4, streams 1 and 3 are warmed as they pass through the heat exchanger, while stream 5 is cooled as its energy is transferred to streams 1 and 3. The equation for the second law efficiency is shown in equation 3.16.

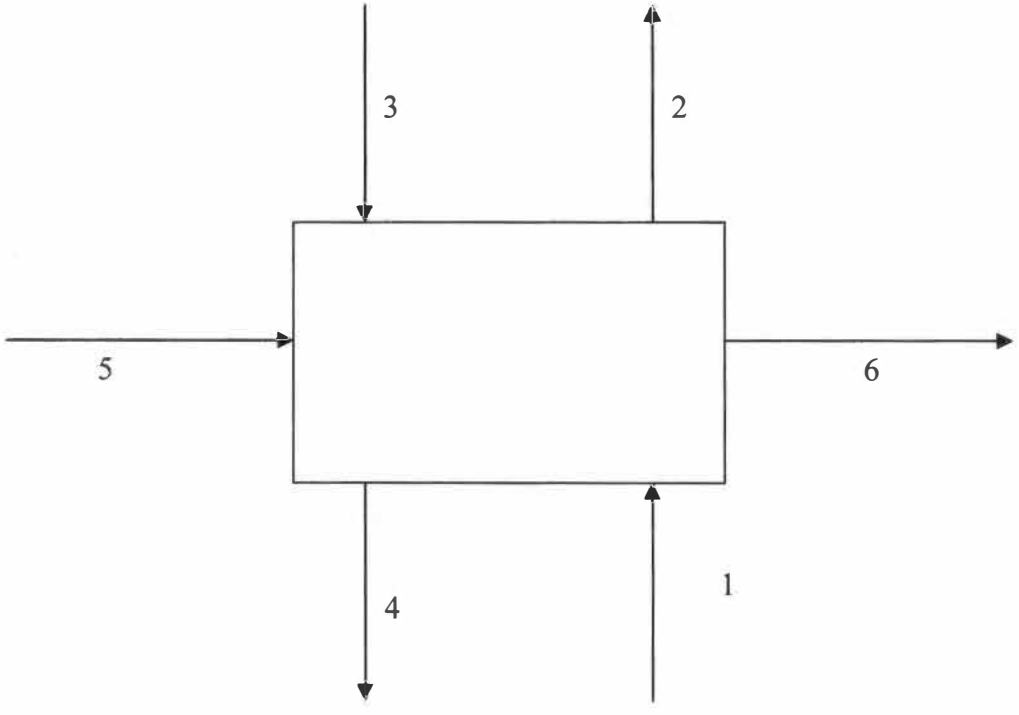

Figure 3.4. Schematic of MATIANT Cycle Central Heat Exchanger

$$\eta = \frac{(\psi_4 - \psi_3) + (\psi_2 - \psi_1)}{\psi_5 - \psi_6} \cdot 100 \tag{3.16}$$

Equation 3.16 shows that the second law efficiency of the central heat exchanger is the ratio of the availability increase in the cold streams to the availability decrease of the warm stream. Equation 3.17 shows the irreversibility associated with the process of warming the working fluid.

$$\dot{I} = \dot{n} \cdot T_o \cdot ((s_4 - s_3) + (s_2 - s_1) - (s_5 - s_6)) \tag{3.17}$$

Note that this equation takes on a different form than the equation that calculates the irreversibility associated with the cooling of the process stream in the intercoolers and condenser. This is because the central heat exchanger does not contain a waste stream, while the condenser and intercoolers do. As mentioned previously, the MATIANT cycle makes no use of the availability added to the cooling medium in the intercoolers and condenser. Therefore, the availability added to these streams is not included in the calculations. The central heat exchanger does not have any waste streams. Because all streams remain a part of the cycle, all inlets and outlets are considered in the calculation of the irreversibility of the component.

Another type of equipment in the MATIANT cycle is a combustion chamber. Figure 3.5 on the following page shows a general diagram for a combustion chamber.

In a combustion chamber, a fuel reacts with an oxidizer (either air or pure oxygen) resulting in products with a different composition than the reactants that have a temperature significantly higher than either of the reactants. The analysis of the combustion chamber must account for both chemical and physical availability. Equation

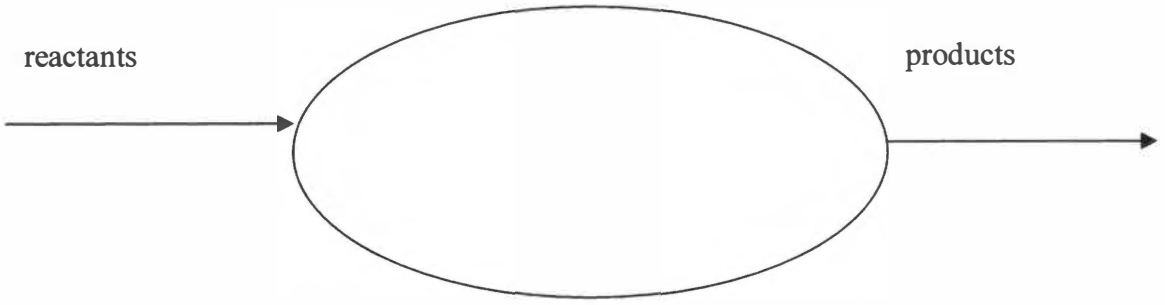

Figure 3.5. Combustion Chamber Schematic

3.18 is the formula for calculating the second law efficiency of a combustion chamber.

$$\eta = \frac{\sum \Psi_{products}}{\sum \Psi_{reactants}} \cdot 100 = \frac{\sum \left(\Psi_{thermomechanical} + \Psi_{chemical}\right)_{products}}{\sum \left(\Psi_{thermomechanical} + \Psi_{chemical}\right)_{reactants}} \cdot 100 \qquad (3.18)$$

Equation 3.19 that shows how the irreversibility can be found.

$$\dot{I} = \sum \Psi_{reactants} - \sum \Psi_{products} \qquad (3.19)$$

The thermomechanical availability is defined in equation 3.19.

$$\psi = \sum_{e}^{N_E} \dot{n}_e \cdot \left(h_e - h_{e,o} - T_o \cdot \left(s_e - s_{e,o}\right)\right) \qquad (3.19)$$

Thermomechanical availability is the availability due to the temperature and pressure of the stream in relation to the dead state. The chemical availability is the maximum theoretical work that can be developed by the reaction of a fuel and an oxidizer. Values for the chemical availability of various substances at environmental conditions are tabulated and easily obtainable for calculation purposes. Moran and Shapiro show two models that can be used to determine the chemical availability of a substance. For this thesis, Model I is used. This model, the gas phase of the reference environment closely correlates to that of the natural atmosphere, while the assumed dead state pressure is

1.019atma [10]. This model is developed by Ahrendts [63]. For a more complete derivation and description of chemical availability, consult Moran and Shapiro [64].

The final component category in the MATIANT cycle is the splitter or phase separator. These components are used to send carbon dioxide to sequestration and to remove condensed water from the process stream, respectively. Figure 3.6 shows a diagram of the equipment now under consideration. Stream 3 can be considered to be the waste stream that does not remain in the process, while stream 2 remains in the cycle. No second law efficiency is associated with these components. However, there is some availability that is "destroyed" in the sense that it is removed from the process. Hence, there is some irreversibility found in these pieces of equipment. The equation that shows how to calculate the amount of availability that exits the cycle, which can also be defined as the irreversibility of the component can be found in equation 3.20.

$$\psi_3 = \dot{n}_3 \cdot \left(h_3 - h_{o,3} - T_o \cdot \left(s_3 - s_{o,3}\right)\right) \tag{3.20}$$

Section 3.4. Parametric Studies. In order to ascertain the impact of various cycle parameters on cycle performance, several parametric studies were performed on the base case model of the MATIANT cycle. The studies were undertaken by varying only a

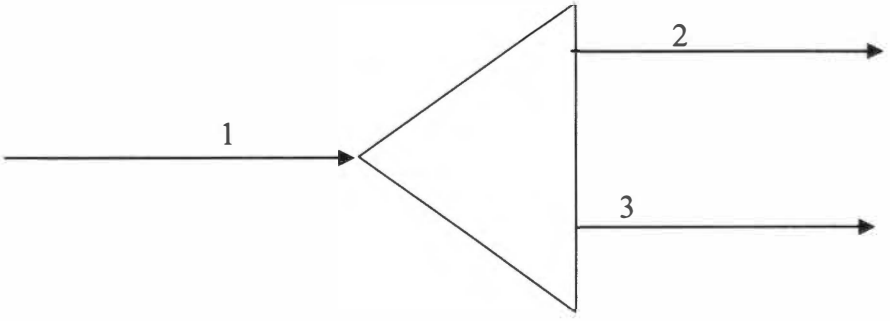

Figure 3.6. Diagram of a Splitter or Phase Separator

single parameter to determine its effect on the MATIANT cycle; all other parameters were left unchanged in the investigation. The parameters of interest were identified based on engineering insight into what cycle parameters are important in a power plant, as well as what inputs into the model can be controlled by the user. The results of the various sensitivities are compared to the base case using the same criteria that are used to analyze the base model: first and second law efficiency, fuel usage and heat rate. Similar to the comparison of the simple cycle power plant to the MATIANT cycle, the power output from the cycle with the changed parameters is not significantly deviated from 250MW. Five different parameters are deemed crucial to vary such that the MATIANT cycle can be better understood: gas line pressure, maximum cycle temperature, oxygen delivery temperature, maximum cycle pressure and intercooler temperature

The base case of the MATIANT cycle uses a gas pressure of 3500kPaa (508psia). This value comes from discussions with employees at Tengasco who communicated this value for the pressure of natural gas in large delivery pipeline. However, it is possible that depending on the location of the actual MATIANT cycle power plant that the gas delivery pressure will be less than this value. By inputting a lower pressure into HYSYS for the natural gas, the significance of gas delivery pressure on overall cycle performance can be observed. In the base case model, the two gas streams are formed into one stream that is split to deliver the fuel to the two combustion chambers. In the varying fuel pressure case, this single fuel stream is made the output from a compressor. The stream pressure is left unchanged at 3500kPaa (508psia), but the temperature, which had been input by the user as 24°C (75°F), is not specified. In Figure 1.10, these changes are made to streams 8 and 11. A new stream is then created and input into the fuel compressor.

For this new stream, the pressure is input as 689.5 and 1379kPaa (100 and 200psia) and the temperature is entered as 24°C (75°F). The compressor polytropic efficiency is set at 80 percent and HYSYS then calculates the work input required by the compressor and the temperature of the outlet stream. This outlet stream is then split, as mentioned earlier, and sent to each combustion chamber.

Literature on the MATIANT cycle lists the maximum cycle temperature as 1300°C (2372°F). This is the temperature of the working fluid exiting both combustion chambers and entering the intermediate and low pressure turbines. Industry experience indicates that this value is approaching the upper limit of current technology. The metallurgy of the turbines and the ability to cool the blades limits the maximum inlet temperature. Therefore, the maximum cycle temperature may turn out to be lower than what is contained in the base case. However, continuing advances in metallurgy and cooling technology may allow for the maximum cycle temperature to exceed what is shown in the base model. Each of these possibilities is considered by varying the maximum cycle temperature, which is found in streams 9 and 13 in Figure 1.10. The inlet temperature for the intermediate and low pressure turbines ranges from approximately 1150°C to 1460°C (2102°F to 2660°F) in this parametric study. Intermediate temperatures within this range were investigated as well. The maximum cycle temperature allowed by the ADJUST blocks in the model is altered by the user to obtain the various exit temperatures from the combustion chambers. HYSYS then proceeds to calculate a converged process with these new maximum cycle temperatures, within the specified tolerances, which are shown earlier in Table 2.2.

Although the proposed MATIANT cycle assumes the presence of a dedicated air separation unit to provide oxygen for combustion, it is possible that the power plant as constructed may receive its oxygen from an air separation unit that supplies oxygen for many customers. In this case, the oxygen will arrive at the MATIANT cycle in a pipeline at ambient temperature rather than at the elevated temperatures found in the base model. The high pressure and low pressure oxygen arrive at 140°C (284°C) in the base case model. In addition, the oxygen delivery pressure may not be what is required by the MATIANT cycle. The temperature of the arriving oxygen, streams 7 and 12 in Figure 1.10, is changed in the model to 24°C (75°F) to allow for a comparison between the assumption that the oxygen comes from a pipeline rather than a dedicated plant. Furthermore, the cycle performance for an oxygen delivery pressure of 344.7kPaa and 689.5kPaa (50psia and 100psia) at 24°C (75°F) is investigated, as is the behavior of the cycle when the oxygen temperature is merely lowered but is available at the pressures required by the MATIANT cycle. Not changing the pressure of the incoming oxygen allows for the impact of this variable on the cycle to be seen without factoring in the inclusion of additional compression power due to the oxygen compressors. When the pipeline pressure of oxygen is 344.7kPaa (50psia), both oxygen streams must be compressed, while an oxygen delivery pressure of 689.5kPaa (100psia) necessitates the use of compression only for the combustion chamber immediately prior to the intermediate pressure turbine. By eliminating the dedicated plant, the power requirements for the air separation unit are also eliminated, thereby raising the net power output from the MATIANT cycle. An alternative is to reduce the output of the various turbines in the process such that net power output from the cycle is approximately

250MW. In this analysis, the turbine output is not changed while the power debit for the air separation unit is eliminated, increasing the net power output from the cycle.

The maximum cycle pressure of the MATIANT cycle plays a key role in determining the power that the plant develops. Although a high pressure allows for more pressure drop, and consequently more power, to be realized in the cycle expanders, it also requires a higher power input to the compression train. It must also be considered that the maximum cycle pressure may have some bearing on the sequestration of the carbon dioxide, as the carbon dioxide removed from the cycle is at maximum pressure. Even though the scope of this project does not include the method employed to sequester the carbon dioxide, the requirements of this process may have to be taken into account in the final design of the cycle. Whatever the final design maximum pressure of the MATIANT cycle is determined to be, some of the compressor power is lost when the high pressure carbon dioxide is removed from the power plant for sequestration. For the parametric study, the maximum cycle pressure is examined at 20000kPaa and 30000kPaa (2901psia and 4351psia) to discover the impact of this input on the overall performance of the cycle. The interstage pressures are also changed such that the compression ratio in each stage of compression is approximately equal. This necessitates changes in the pressure for statepoints 20, 22, 24 and 1 in Figure 1.10. Additionally, the pressure of stream 4 as it exits the central heat exchanger is adjusted to reflect a two percent pressure drop through the heat exchanger, which is the same pressure drop that is included in the model of the base case MATIANT cycle. For the case where the maximum cycle pressure is 30000kPaa (4351kPaa), the third intercooler exhaust temperature is set at 40°C (104°F). Stream 24 therefore has this elevated temperature. This is because the working fluid

condenses at 30°C (86°C) when cooled after the third compression stage. In order to keep the working fluid in the vapor phase, the outlet temperature from this intercooler is raised.

Power can be saved in any compression train by employing intercooling between compressor stages. For the same compression ratio of a given fluid, less power is required to compress a low temperature inlet stream than a high temperature inlet stream. For this reason, the proposed MATIANT cycle includes three stages of intercooling such that the cycle begins to approach the performance of an ideal Ericson cycle, where compression is accomplished at a constant temperature. The base case MATIANT cycle model assumes that intercooling reduces the temperature of the working fluid to 30°C (86°F). In practice, the actual temperature exiting the intercoolers depends on the location of the plant, the cooling medium used and an economic study of the acceptable size of the intercoolers. Varying the outlet temperature from the intercoolers allows for the impact on cycle performance of this intermediate temperature to be studied. In the model, the temperature of the process fluid exiting each intercooler is changed to the desired temperature and HYSYS performs the necessary calculations to converge the model. The cycle performance at interstage temperatures of 35°C, 40°C, 45°C and 50°C (95°F, 104°F, 113°F, 122°F) is therefore examined and compared to the base case. The temperature for streams 21, 23 and 25 in Figure 1.10 are altered in this parametric study. In addition to changing the outlet temperature from the intercoolers to the aforementioned temperatures, the outlet temperature from the condenser, stream 17 and point *n* in Figure 1.10, is changed to equal the outlet temperature from the intercoolers.

Section 3.5. Alternative Method of Removing Water Vapor. Besides lowering the compression power required, intercoolers between the compressor stages allow for residual water to be taken out of the process by condensing the water, which is then removed in phase separators. The removal of the water is necessary to prevent a liquid from entering any of the compression stages after compression and intercooling. Furthermore, water is removed to prevent it from being present in the sequestration stream of carbon dioxide. The model under consideration does this primarily by condensing the stream exiting the low pressure expander (point *n* in Figure 1.10) and by then removing remaining water that is condensed in the intercoolers in the compressor train. Although a condenser is present upstream of the compression train to remove water from the process, it is determined by manipulating the HYSYS model that the stream must be cooled to -11°C (12.2°C) at statepoint 17 in Figure 1.10 to reduce the water content in the process stream to the same level as the base case MATIANT cycle achieves by reducing the working fluid to 30°C (86°F) in the condenser and interstage coolers. Both of these methods reduce water content to below two tenths of one percent. To reach this temperature, it is clear that refrigeration must be used. A model refrigeration cycle is constructed in HYSYS to cool the carbon dioxide-water mixture down to this temperature. Figure 3.7 depicts this process. The working fluid, stream 1, is first cooled down to near ambient temperature, 30°C (86°F), in a heat exchanger using air or water. Stream 1 is the same as stream 16 in Figure 1.10. Stream 2 is an intermediate stream not present in Figure 1.10 that subsequently enters a heat exchanger where the

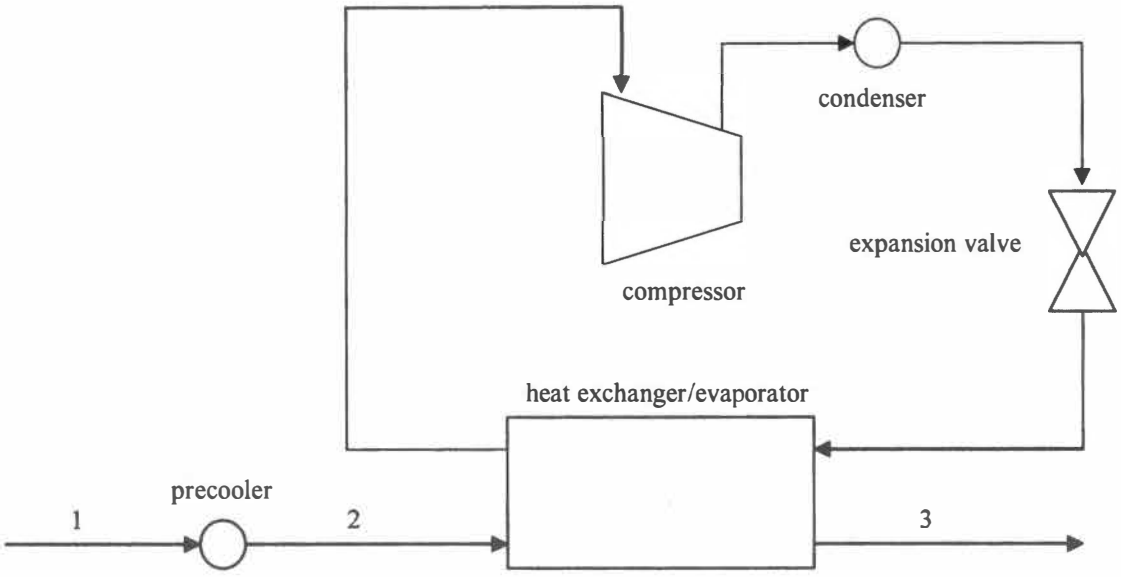

Figure 3.7. Schematic of Refrigeration Process to Remove Water from MATIANT Cycle

cooling medium is a refrigerant that is contained in closed loop refrigeration cycle containing compression, Joule-Thomson expansion and heat rejection. In this model, the refrigerant is R-134a. Stream 3 exiting the heat exchanger corresponds to stream 17 in Figure 1.10. The temperature of this stream is -11°C (12.2°F). Although refrigeration requires power, the working fluid will enter the compression train at a significantly lower temperature than in the base case. This study compares a model with a refrigeration cycle to the base case. Intercooling is still present in the compressor train, but its sole purpose is to lower the compression power, not to remove residual water. The outlet temperature from the intercoolers is kept at 30°C (86°F).

This study is extended by noting that refrigeration may be considered because of the temperature of the available cooling medium at the location of the power plant. The viability of employing refrigeration at elevated intercooling temperatures can be ascertained by varying the interstage temperature in the compression train. In addition,

the temperature of the working fluid entering the refrigeration process is varied to match the interstage temperature that can be realized. The cycle performance is evaluated when temperature that can be reached by using an available environmental cooling medium is set at 40°C, 45°C and 50°C (104°F, 113°F, 122°F) for streams 21, 23 and 25 in Figure 1.10. These results are then compared to the performance of the MATIANT cycle without refrigeration and the same intercooler exit temperatures.

Section 3.6. Additional Stage of Compression. As has been mentioned previously, the use of interstage cooling in the compression train serves to lower the overall compression power requirements. The practice of intercooling removes heat of compression from the process and allows the working fluid to be compressed at a lower temperature. For a given compression ratio, the power requirement decreases as the compressor inlet temperature decreases. In order to better determine cycle behavior, the effect of an additional stage of intercooling, water removal and compression is added to the base case of the MATIANT cycle such that there are now five stages of compression and four stages of intercooling and water knockout. The additional compressor is set to have the same polytropic efficiency as the other compressors in the process: 80 percent. In addition, the outlet pressure from the compression train is maintained at 25600kPaa (3713psia), while the compression ratio in each stage is reduced to ensure that the final temperature requirement is met. The exit temperature in the added intercooler is also set to be 30°C (86°F), the same as in the already existing intercoolers. The performance parameters of this configuration are then compared to those of the base case MATIANT cycle to determine the impact on cycle performance of adding a compression stage.

Chapter 4. Results and Conclusions

Section 4.1 Summary of Analytical Methods. Subsequent to the determination of the parametric studies to be performed on the MATIANT cycle, the models are input into HYSYS to ascertain the impact of varying the values of temperature and/or pressure at certain cycle statepoints. The results generated by HYSYS are fed into an EXCEL spreadsheet and used to determine first law and second law efficiency and the heat rate of the parametric study. The power requirements for each compressor stage are taken from HYSYS, as is the power output from each expansion stage. HYSYS also determines the amount of fuel needed by the MATIANT cycle in each case. The fuel usage is used to find the heat rate, first law efficiency and to scale the power consumed by the air separation unit compared to the base case. The known power requirement for the air separation unit is multiplied by the ratio of the fuel needed in the parametric study to the fuel needed in the base case to arrive at the power draw for the air separation unit in each parametric study. The power from the base case air separation unit is provided by a HYSYS model. The design of the air separation unit is described in the Appendix of this thesis. The compressor and air separation unit power inputs are subtracted from the expander output to calculate the net power output of the MATIANT cycle. This number is used to determine the first law efficiency by dividing it by the product of the fuel usage and the higher heating value of the fuel. To calculate the second law efficiency, the molar flow rate, molar enthalpy and molar entropy of each stream entering and exiting a combustion chamber are required from HYSYS. These numbers are used to find the availability added in the combustion chambers as laid out in equations 3.8 and 3.9. To find the second law efficiency, the net power output from the plant is divided by the

availability increase in the combustion processes. The analysis of the simple cycle model uses the same logic as the parametric studies on MATIANT cycle to establish its performance. The tables contained in this chapter will not show the fuel usage and power inputs or outputs used in the analysis. Only the first and second law efficiency and heat rate are found in this chapter, as they are the basis on which the MATIANT cycle is judged against a simple cycle and the altered MATIANT cycles. Where appropriate, a deeper study of certain parametric studies includes a consideration of the turbomachinery, but this is not standard practice. The Appendix to this thesis contains a comprehensive table used to analyze the MATIANT cycle.

For the component study on the MATIANT cycle, the power inputs and outputs for the compressors and turbines, respectively, are taken from HYSYS. Also, the flow rate, enthalpy and entropy values for each stream are provided by HYSYS. These values are used in concert with equation 3.11 through equation 3.20 to achieve the irreversibility and second law efficiency of each component in the MATIANT cycle. This chapter will only reveal the performance results of each component. The Appendix to this thesis should be consulted for intermediate values used to calculate the irreversibility and second law efficiency associated with each component of the process.

Section 4.2. Parametric Studies. This section lays out the results of the parametric studies performed on the MATIANT cycle. A description of each study can be found in section 3.4 of this thesis. Figure 4.1 shows a temperature-entropy diagram of the base case MATIANT cycle. The statepoints in the figure corresponds to those shown in Figure 1.10. This figure not only provides a visual presentation of the cycle performance but also serves to provide a graphic that can be used to describe the changes

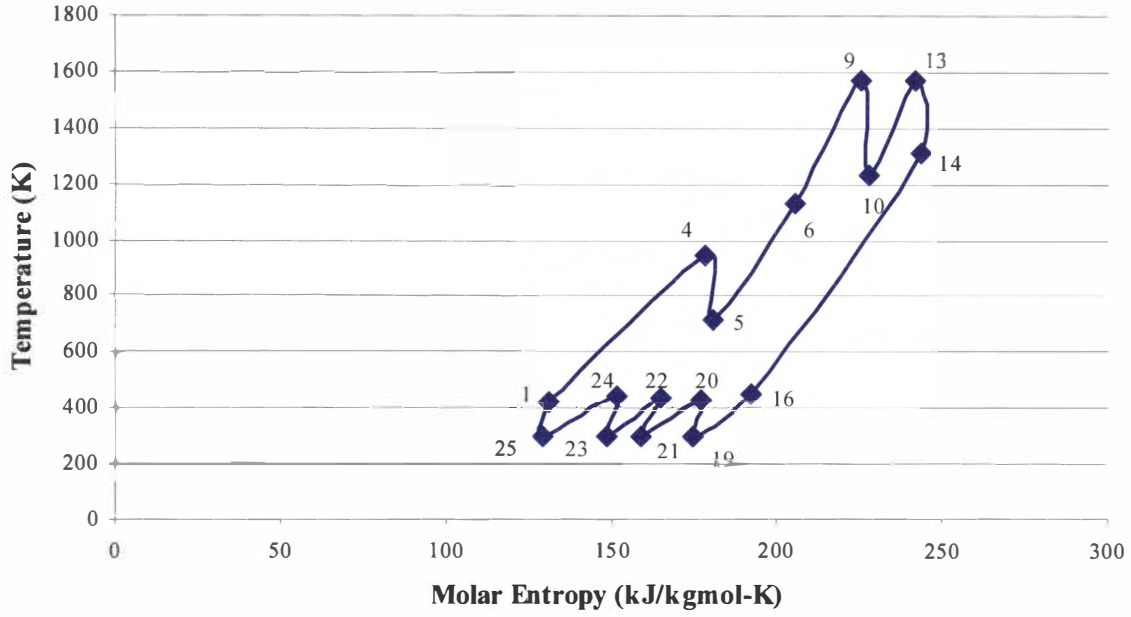

Figure 4.1. Temperature-Entropy Diagram for the MATIANT Cycle

in performance that are observed when certain parameters in the MATIANT cycle are varied. Moran and Shapiro state that for any closed system undergoing an internally reversible process, the area underneath the temperature-entropy curve represents the energy transfer by heat. Furthermore, for a Carnot power cycle, which has four internally reversible processes, it can be shown that the first law efficiency can be found by simply knowing the maximum and minimum cycle temperatures in absolute terms. Equation 4.1 shows this relationship.

$$\varepsilon = 1 - \frac{T_{min}}{T_{max}} \tag{4.1}$$

Equation 4.1 represents the maximum efficiency that is achievable for a given power cycle. The complete derivation of this formula can be found in Moran and Shapiro [65].

Although the MATIANT cycle does not have internally reversible processes, a consideration of the temperature-entropy curve is still useful when changing cycle parameters and the qualitative impact, if there is one, of the parametric studies on the curve shown in Figure 4.1 are cited.

Section 4.2.1. Varying Fuel Pressure. The performance characteristics of the MATIANT cycle when the incoming fuel pressure is changed to reflect differing pipeline delivery pressures can be found in Table 4.1.

When the fuel delivery pressure is 1379kPaa (200psia), the fuel compressor power input is 2.2MW. If the fuel delivery pressure is decreased to 689.5psia, the fuel compressor power increases to 4.3MW. As the table shows, the first law efficiency and second law efficiency both decrease if fuel compression is required, but the drop is not significant. While this alteration to the process has no direct impact on the temperature-entropy diagram of the MATIANT cycle in Figure 4.1, it does decrease the net work the cycle produces.

Table 4.1 shows that decreasing the fuel pressure from 1379kPaa (200psia) to 689.5kPaa (100psia) has no discernable impact on cycle performance. The reason for this can be found in the fact that cycle convergence is based on a range of maximum temperatures and power outputs, as shown in Table 2.2. In the case of the lower fuel delivery pressure, the inlet temperatures to the intermediate and low pressure turbines are higher than for the elevated fuel pressure. Consequently, the turbine output is higher and offsets the increased compression power required, leading to a situation where the results are the same for different fuel pressures. As mentioned earlier, the overall impact is slight regardless of the fuel supply pressure.

Table 4.1. Performance Characteristics for Varying MATIANT Cycle Fuel Pressure

	first law efficiency--HHV (%)	second law efficiency--(%)	heat rate (kJ/kWh)
base case, Fuel P=3500kPaa	39.3	58.0	9154.4
Fuel P=1379kPaa	39.0	57.7	9233.6
Fuel P=689.5kPaa	39.0	57.5	9233.6

The results shown above could be improved slightly by adding two fuel compressors to supply the fuel at two different pressures rather than one as is done in this model. As fuel is required by the MATIANT cycle at two different pressures, a dedicated compressor for each pressure could be used rather than pressuring both streams to 3500kPaa (508psia). However, given the small performance debit, this is not a major concern. Economics play a role in this decision, as the additional capital investment and maintenance costs required for a second compressor may not be recovered by the small performance enhancement gained in the process.

Section 4.2.2. Varying Maximum Cycle Temperature. The impact of varying the combustion temperature on the performance of the MATIANT cycle can be found in Table 4.2. By increasing the maximum cycle temperature, the peaks in Figure 4.1, points 9 and 13 are raised. Equation 4.1 predicts a higher Carnot cycle efficiency, as the minimum temperature is not changed while the maximum temperature increases. On the other hand, if the maximum temperature is lowered, these peaks are lowered in the figure. Because the maximum cycle temperature is decreased, equation 4.1 predicts that the Carnot cycle efficiency will also decrease. In Figure 4.1, statepoints 10 and 14 are also impacted by a change in the maximum cycle temperature, but the effect of this on the diagram is not as significant as the impact of raising points 9 and 13.

Table 4.2. Performance Characteristics for Varying MATIANT Cycle Maximum Temperature

	first law efficiency--HHV (%)	second law efficiency--(%)	heat rate (kJ/kWh)
base case Max T=~1300°C	39.3	58.0	9154.4
Max T=~1460°C	41.7	58.1	8613.7
Max T=~1370°C	40.4	58.1	8914.9
Max T=~1330°C	39.7	58.1	9061.7
Max T=~1260°C	38.7	57.9	9295.1
Max T=~1225°C	38.1	57.7	9456.6
Max T=~1150°C	36.5	57.6	9858.4

Table 4.2 reveals that as the maximum cycle temperature is increased, the first law efficiency increases. The second law efficiency is higher in this case, but is for all practical purposes constant. The heat rate can be seen to decrease in this scenario. Conversely, as the temperature exiting the combustion chambers decreases, the first law efficiency goes down and the second law efficiency, while decreasing slightly, also remains essentially constant. As the first law efficiency decreases, it is observed that the heat rate increases. Clearly, significant gains in first law performance of the MATIANT cycle can be realized if it is possible to increase the combustion temperature. Figure 4.2 on the following page shows graphically the relationship between combustion temperature and the first law efficiency of the MATIANT cycle. The reason for the increase is that the power output from an expander is directly related to the inlet temperature. Figure 4.3 shows that the specific power of the low and intermediate pressure turbines increases as the inlet temperature is increased.

It may seem somewhat counter-intuitive to see the first law efficiency of the MATIANT cycle varying greatly with the combustion temperature while the second law

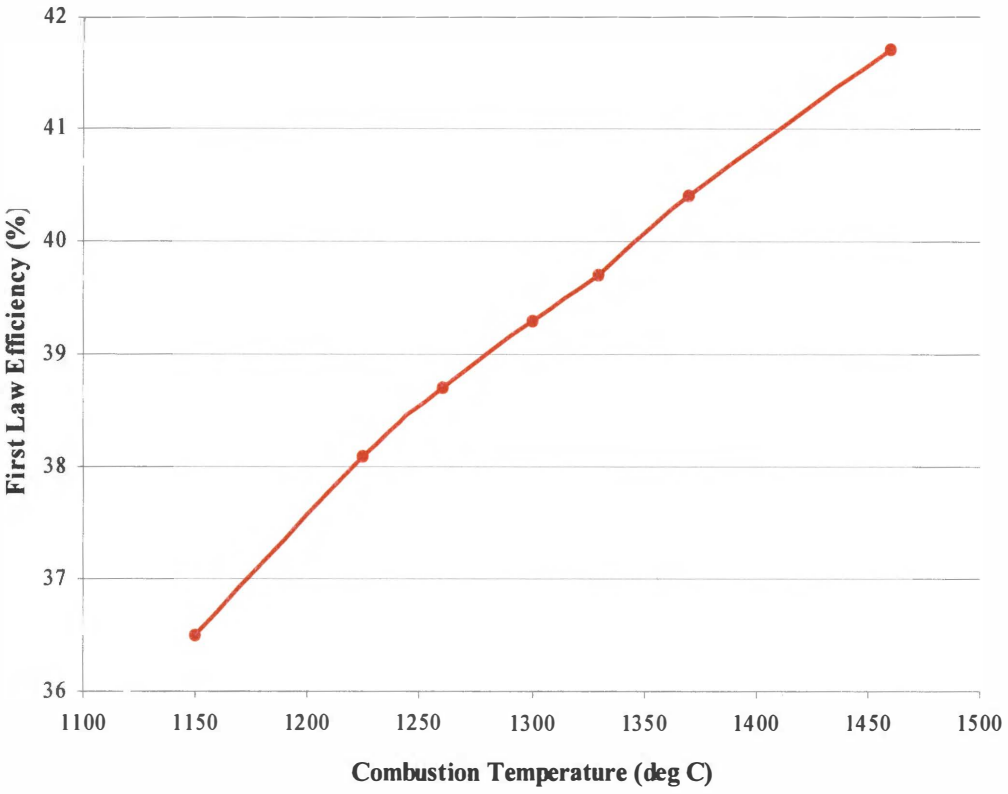

Figure 4.2. Impact of Combustion Temperature on MATIANT Cycle First Law Efficiency

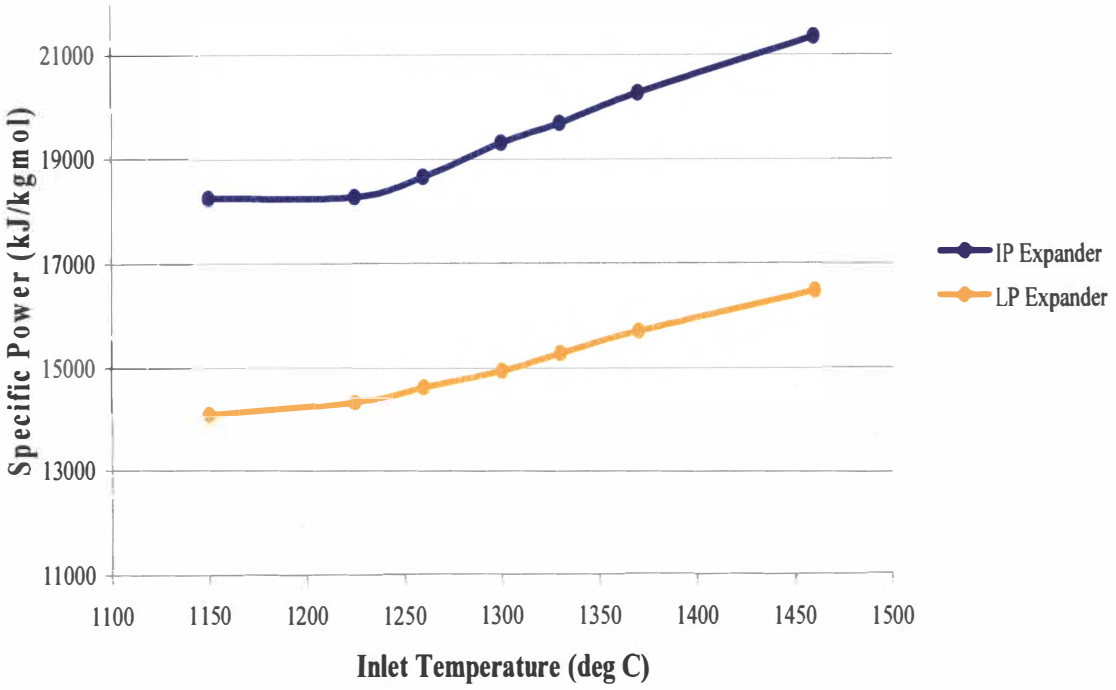

Figure 4.3. Impact of Turbine Inlet Temperature on Turbine Specific Power

efficiency remains effectively constant. Some insight into this can be gained by noting that stream 6 in Figure 1.10 serves as a heat sink in the combustion process by absorbing some of the heat of combustion such that the exit temperature from the combustion chamber is in line with what is specified by the user. As the combustion temperature increases, the flow rate of stream 6 is decreased accordingly so that less heat is absorbed into this stream. Consequently, the compression power decreases as the combustion temperature increases because the flow rates are lower. At the same time, the output from the turbines decreases because the flow rate through the equipment is decreasing. This decrease is offset by a higher inlet temperature, which leads to the increase in specific power as Figure 4.3 displays. An analysis of the compressor power input and turbine power output reveals that the decrease in turbine power output is less than the

decrease in compressor power input. The net result of this is that the net power of the MATIANT cycle increases as the combustion temperature increases. However, it is also worth noting that the availability input in the combustion chambers increases as combustion temperature increases. This is in line with expectations, as a higher temperature denotes a higher availability. The increase in net power is therefore counterbalanced by the increase in availability input in the combustion chambers, leading to no net change in the second law efficiency. In addition to the above considerations, it will be shown later that in the combustion chambers destroy the most availability of any component in the MATIANT cycle. Therefore, the higher availability that accompanies the higher temperature also means that there are more losses. These additional losses act to decrease the second law efficiency as the combustion temperature increases.

Section 4.2.3. Varying Oxygen Delivery Conditions. Table 4.3 displays the results achieved when the oxygen delivery conditions are altered, distinguishing between retaining the air separation unit power requirements and eliminating them for the purpose of comparison. By keeping the air separation unit, the impacts of changing the oxygen conditions can be isolated. It is reasonable to assume that if oxygen is provided by a pipeline, then the dedicated air separation unit that supplies oxygen to the MATIANT cycle is done away with, along with the sizeable power input it takes from the MATIANT cycle. However, because it is useful to see what a change in parameter does to the base case MATIANT cycle, the results are presented both with and without an air separation unit. This allows for the impact of changing the oxygen delivery conditions on base case performance to be appreciated as well as the overall influence of removing the air separation unit and changing the oxygen temperature and pressure.

Table 4.3. Performance Characteristics for Varying MATIANT Cycle Oxygen Delivery Conditions

	first law efficiency--HHV (%)	second law efficiency--(%)	heat rate (kJ/kWh)
base case O_2 T=140°C, p=3500kPaa and 500kPaa	39.3	58.0	9154.4
O_2 T=24°C, p=344.7kPaa, no ASU	46.6	68.7	7718.6
O_2 T=24°C, p=344.7kPaa	38.1	56.2	9450.0
O_2 T=24°C, p=689.5kPaa, no ASU	47.0	69.4	7661.1
O_2 T=24°C, p=689.5kPaa	38.4	56.8	9363.9
O_2 T=24°C, no ASU	47.5	70.3	7585.7
O_2 T=24°C	38.9	57.6	9252.7

Simply decreasing the oxygen temperature lowers the first and second law efficiency of the MATIANT cycle by a small amount. However, when the air separation unit is taken out of the equation, cycle performance jumps significantly. This assumes that oxygen is available at the pressures required by the MATIANT cycle. If the oxygen requires compression, the performance of the MATIANT cycle diminishes as the delivery pressure is lowered. Table 4.3 shows that the first law efficiency decreases by one percent or more under the conditions investigated. However, when the air separation unit is removed from consideration, the performance is improved greatly, as the first law efficiency increases by almost eight percent and the second law efficiency increases by more than ten percent. Like varying the fuel pressure, none of these changes directly impacts temperature entropy diagram in Figure 4.1. However, they do impact the net work output of the MATIANT cycle.

Section 4.2.4. Varying Maximum Cycle Pressure. The performance comparison between the base case MATIANT cycle and the cycle with varying maximum pressure is shown in Table 4.4.

The table shows that first law efficiency decreases for both cases where the maximum cycle pressure is decreased or increased. However, when the pressure is decreased, the second law efficiency increases slightly while it decreases when the maximum cycle pressure is increased. Section 3.4 notes that in the case where the maximum cycle pressure is 30000kPaa (4351psia), the exit temperature from the third intercooler is increased to 40°C (104°F) to avoid liquefaction of the carbon dioxide after the third stage of compression. The fact that the interstage temperature is higher in the higher pressure case is not insignificant and will be taken into account in the future. In general, raising the maximum cycle pressure will raise points 20, 22, and 24 on the diagram in Figure 4.1. This decreases the area contained in the curve, which represents a decrease in the net work produced by the cycle, as described in Moran and Shapiro [66]. At the same time, some additional area is gained back because the entropy at states 4 and 5 is decreased and the temperature at state 5 decreases. If the maximum pressure is lowered, points 20, 22 and 24 go lower in the figure, which increases the area or net cycle

Table 4.4. Performance Characteristics for Varying MATIANT Cycle Maximum Pressure

	first law efficiency--HHV (%)	second law efficiency--(%)	heat rate (kJ/kWh)
base case Max P=25600kPaa	39.3	58.0	9154.4
Max P=20000kPaa	38.9	58.1	9252.7
Max P=30000kPaa	38.5	56.5	9360.7

output. However, an entropy increase at statepoints 4 and 5 and a temperature increase at state 5 reduces the area gained by lowering the maximum cycle pressure.

When the maximum cycle pressure is 20000kPaa (2901psia), the compressor power requirement is lowered by 5.7MW, while the turbine output decreases by 8.3MW. On the other hand, for a maximum cycle pressure of 30000kPaa (4351psia), the compressor power input is increased by 5.3MW while the turbine output remains unchanged. In both cases there is a change in the power output in the high pressure turbine. Section 3.4 notes that in this parametric study, the statepoint pressure values are changed for the compressor exit streams and the exit stream from the central heat exchanger (stream 4 in Figure 1.10). No other pressures are changed, which indicates that the power output from the intermediate and low pressure turbines should be relatively unaffected. For the lower maximum cycle pressure, the inlet pressure to the high pressure turbine is lower, so the pressure drop and therefore the power output is less. Conversely, the turbine power output is increased for the higher pressure case because the elevated inlet pressure leads to a larger pressure drop in the turbine and consequently more power. Table 4.5 compares the power output from the high pressure expander for the three cases and also shows the specific power. The specific power is used to compare

Table 4.5. High Pressure Expander Output for Varying Maximum Cycle Pressure

	HP expander power output (MW)	**HP expander specific power (kJ/kgmol)**
Base case Max P=25600kPaa	117.4	11692
Max P=20000kPaa	98.5	10350
MaxP=30000kPaa	119.5	12530

the three cases because it eliminates changes in the flow rate of the working fluid through the turbine. The inlet pressure to this machine is two percent lower than the maximum cycle pressure, as specified in the model of the MATIANT cycle.

Another point of interest is the specific power consumption for each compressor stage. Table 4.6 shows these values. Before viewing the table, it can be concluded that the specific power decreases as the maximum cycle pressure decreases and increases for increasing cycle pressure. This should particularly be true for the 30000kPaa (4351psia) case where the exit temperature from the final intercooler is higher than the base case. In general, the table supports this conclusion. However, Table 4.6 shows that in the fourth stage of compression, the base case has a lower specific power input than the parametric study with a lower maximum pressure. Furthermore, the fourth stage specific power is appreciably lower than that of the other three stages for each case. The reason for this can be found by looking into the property details of the fourth stage compressor provided by HYSYS. Taking the base case, it can be determined that the density of the inlet stream to the fourth stage (stream 24 in Figure 1.10) is $195.9\,{}^{kg}/_{m^3}$. For comparison, the

Table 4.6. Compressor Stage Specific Power for Varying Maximum Cycle Pressure

	First stage specific power (kJ/kgmol)	Second stage specific power (kJ/kgmol)	Third stage specific power (kJ/kgmol)	Fourth stage specific power (kJ/kgmol)
Base case Max P=25600kPaa	5018	5238	4918	3454
Max P=20000kPaa	4952	4898	4623	3603
Max P=30000kPaa	5411	5315	4947	3765

inlet density to the third stage is 29.9 $^{kg}/_{m^3}$. This significant increase in density explains in part the lower power required by the fourth stage compressor for approximately the same compression ratio as the other three compressor bodies. A constant mass flow rate through the compression train, minus a small liquid water dropout, means that for an increased density, the volumetric flow rate is lower. A denser fluid requires less power to increase its pressure compared to a fluid with less density. HYSYS also shows that the heat capacity of stream 24 is 119.3 $^{kJ}/_{kgmol-C}$, while stream 22 entering the third stage compressor has a heat capacity of 42.6 $^{kJ}/_{kgmol-C}$. From this it can be said that the fluid being compressed in the fourth stage can receive more heat of compression before a change in its temperature is realized. A lower temperature translates to less compression power, a result which will be derived later in this chapter. This also serves to decrease the power requirement in the fourth stage compressor. The reason for this behavior can be explained by noting that the compressibility factor of stream 24 is 0.56, while the compressibility factor for stream 22 is 0.91. The inlet stream to the fourth stage compressor is therefore greatly deviating from ideal gas behavior. For stream 24, the boiling point is 24°C (75°F). The temperature of stream 24 is 30°C (86°F). Therefore, the increased density and heat capacity of stream 24 is due to the fact that it is approaching its dew point. A well- known principle can perhaps best sum up the phenomenon observed in the fourth stage of compression: it requires less power to increase the pressure of a liquid than it does to increase the pressure of a vapor, assuming the same substance with the same inlet and outlet pressures. While the fluid entering the

fourth stage compressor is still a vapor, its properties are approaching those of a liquid and the compression power is consequently greatly decreased relative to the other stages of compression.

Another point to be addressed from Table 4.6 is that the specific power increases from stage one to stage two for the base case. This is because the pressure ratio in the first stage of compression is slightly less than the compression ratio in the second stage. While the compression ratio in the first stage is 3.8, the compression ratio in the second stage is 4.1. This is merely the result of the model, as in the model the exit pressure from each compressor body is set so that the compression ratio is four (100kPaa to 400kPaa, 400kPaa to 1600kPaa, etc). Refer to section 2.2 for more details on this. In the MATIANT cycle, the pressure entering the first stage of compression is 105kPaa (15.2psia), meaning that the compression ratio is less than four. Furthermore, the compression ratio in the following stages is slightly greater than four, as the pressure of the working fluid drops in the intercoolers. Therefore, the difference in the pressure ratio between the first and second stage accounts for the unexpected increase in compressor specific power between the first and second stage compressors.

A final point to be addressed from Table 4.6 concerns the small difference in the specific power between the second and third stages of the base case and higher maximum pressure case. Because the pressure ratios are almost equal in these stages for each case, the specific powers are nearly identical. For the base case, the pressure ratio is 4.1 in the second and third stages. In the same stages in the 30000kPaa (4351psia) case, the pressure ratio in the second and third stages is 4.16. This small difference in the pressure ratio accounts for the small difference in specific powers between the two cases.

Section 4.2.5. Varying Intercooler and Condenser Exit Temperature. For an intercooler and condenser exit temperature varying from 30°C (86°F) to 50°C (122°F) in 5°C (9°F) increments, Table 4.7 reveals the changing cycle performance. The main impact of raising the intercooler temperature on Figure 4.1 is to raise the bottom of the cycle, points 19, 21, 23 and 25, which decreases the area contained in the curve. In addition, raising the intercooler temperature increases the minimum cycle temperature, which equation 4.1 shows will lower the cycle efficiency.

From Table 4.7, it can be deduced that increasing the intercooler exit temperature, and thus the compressor inlet temperature has an adverse impact on all facets of cycle performance. These findings are in line with expectations, as a higher compressor inlet temperature indicates a higher compression power. Assuming an ideal gas undergoing an isentropic process, it is known that the temperature is a function of the pressure ratio and specific heat ratio. Equation 4.2 shows this relationship.

$$T_2 = T_1 \cdot \left(\frac{P_2}{P_1}\right)^{k-1/k} \tag{4.2}$$

In equation 4.2, absolute temperatures are used. As the equation shows, a higher T_1 leads to a higher T_2 for the same pressure ratio and specific heat ratio. For an ideal gas, the

Table 4.7. Performance Characteristics for Varying MATIANT Cycle Intercooler and Condenser Exit Temperature

	first law efficiency--HHV (%)	second law efficiency--(%)	heat rate (kJ/kWh)
base case Inter T=30°C	39.3	58.0	9154.4
Inter T=50°C	35.5	52.6	10137
Inter T=45°C	36.2	53.4	9953.8
Inter T=40°C	37.2	55.0	9671.7
Inter T=35°C	38.2	56.4	9432.7

power is a function of the change in temperature, the heat capacity and the flow rate. Equation 4.3 displays this formula on a mass basis, assuming a constant specific heat value.

$$\dot{W} = \dot{m} \cdot c_p \cdot (T_2 - T_1) \tag{4.3}$$

Substituting equation 4.2 into equation 4.3 yields equation 4.4.

$$\dot{W} = \dot{m} \cdot c_p \cdot T_1 \cdot \left(\left(\frac{P_2}{P_1} \right)^{k-1/k} - 1 \right) \tag{4.4}$$

Equation 4.4 clearly shows that a higher inlet temperature results in a higher power requirement for the same compression ratio. Therefore, the results seen in Table 4.7 are to be expected. Table 4.8 shows the impact of the intercooler temperature on the stage specific power for the MATIANT cycle. The preceding logic is found in Moran and Shapiro [67].

Figure 4.4 on the following page shows the behavior of the first law efficiency

Table 4.8. Compressor Stage Specific Power for Varying Maximum Cycle Pressure

	First stage specific power (kJ/kgmol)	Second stage specific power (kJ/kgmol)	Third stage specific power (kJ/kgmol)	Fourth stage specific power (kJ/kgmol)
Base case T=30°C	5018	5238	4918	3454
Inter T=35°C	5103	5330	5020	3707
Inter T=40°C	5178	5423	5122	3928
Inter T=45°C	5267	5578	5223	4122
Inter T=50°C	5267	5599	5319	4298

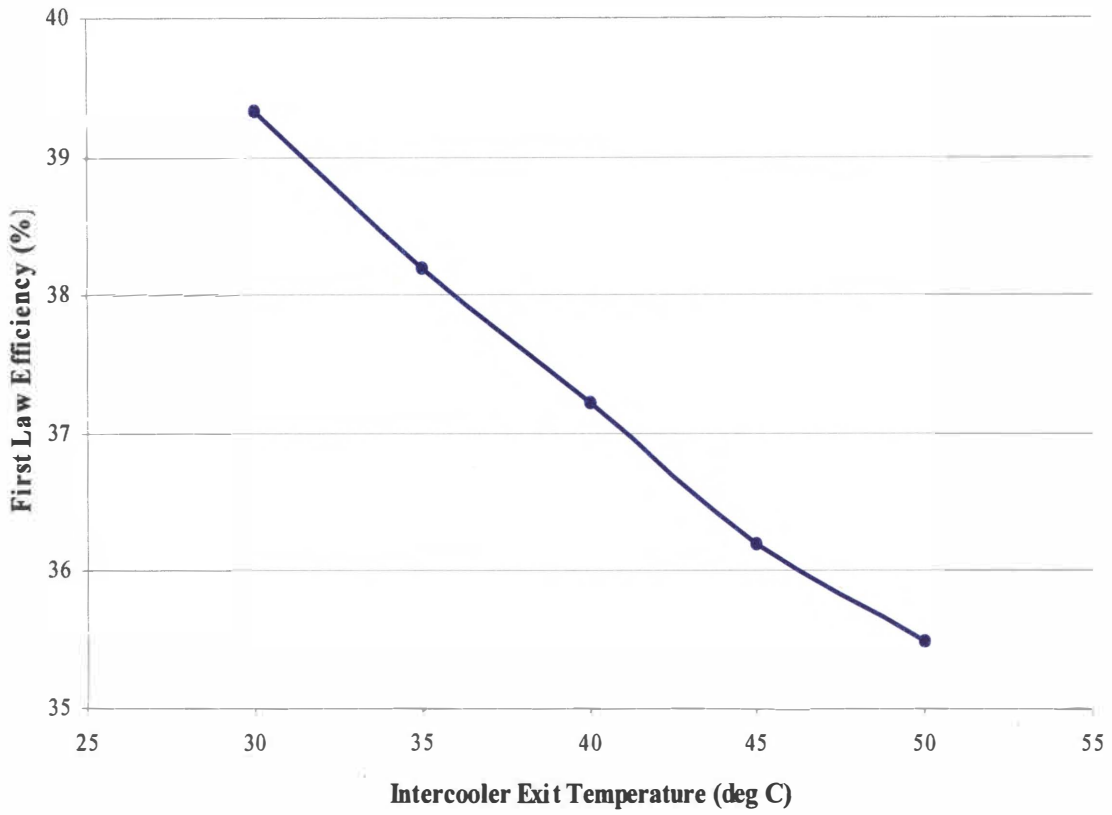

Figure 4.4. Effect of Varying Intercooler Exit Temperature on First Law Efficiency

when the intercooler and condenser exit temperatures are varied. As can be seen in the figure, the first law efficiency decreases with increasing temperature. This is because the compressor power increases as described above while the turbine power remains constant, thereby decreasing the net cycle power and therefore the first law efficiency. Recalling the findings from the varying maximum cycle pressure case, when the maximum cycle pressure is 30000kPaa (4351psia), the intercooler exit temperature is increased to 40°C (104°F) in the third intercooler to prevent carbon dioxide condensation in the process. By doing this, performance results compared to the base case are biased against the higher pressure case because the compressor inlet temperature is higher. It is therefore valuable to compare the case where the maximum pressure is 30000kPaa

(4351psia) to the case where the maximum pressure is 25600kPaa (3713psia), where the intercooler and condenser exit temperature is 40°C (104°F) in both cases. Table 4.9 addresses this evaluation.

Reviewing the results in Table 4.9 shows that the difference in performance between the two cases to be less than the performance difference shown in Table 4.4. This is particularly true concerning the second law efficiency and heat rate. The difference in heat rate is reduced from 2.2 percent to 1.1 percent while the difference in second law efficiency goes from 1.5 percent to 0.9 percent. While the base case maximum pressure still provides better performance, this study goes to show that the temperature to which the working fluid can be cooled in the intercoolers and condenser should play a role in the selection of the maximum pressure realized in the cycle.

Section 4.2.6. Parametric Study Conclusions. By varying certain inputs into the MATIANT cycle model, it is possible to uncover trends and areas for further study in the process. Moreover, it is possible to determine where to direct efforts to improve cycle performance as well as those areas that do not have a major impact on cycle behavior. For example, the fuel delivery pressure does not have a significant impact on the performance of the MATIANT cycle, as modeling different pressures in HYSYS

Table 4.9. Comparison of Base Case Maximum Pressure to Elevated Maximum Pressure for Intercooler Exit Temperature of 40°C (104°F)

	first law efficiency--HHV (%)	second law efficiency--(%)	heat rate (kJ/kWh)
Max P=25600kPaa, Inter T=40°C	37.2	55.0	9671.7
Max P=30000kPaa, Inter T=40°C	36.8	54.1	9786.3

reveals that the same cycle performance is possible whether the pressure is 689.5kPaa (100psia) or 1379kPaa (200psia). Consequently, this is not an area where major performance improvements can be realized.

Similarly, no effort should be directed in revisiting the air separation unit to change the delivery temperature of oxygen, as there is not a significant performance debit associated with lowering the temperature of the incoming oxygen. However, this also goes to prove that if changes in the air separation process result in changes in the oxygen delivery temperature from the facility, the MATIANT cycle will not experience a deleterious change in its performance. In addition, this study reveals that if the oxygen is to come from a pipeline, the delivery pressure is not a major variable in overall MATIANT cycle performance. Table 4.3 confirms this by showing that the variance in the first law efficiency when the oxygen delivery pressure is changed from 344.7kPaa (50psia) to 689.5kPaa (100psia) is less than 0.5 percent. Where effort should be directed is determining whether the oxygen should come from a pipeline or be supplied by an air separation unit dedicated to providing the oxygen needs of the MATIANT cycle. First law efficiency increases of up to eight percent are possible if there is not a power deduct for the air separation unit. The factors in making this determination are economic, as the costs for an oxygen supply contract may be greater than the revenue coming from the additional power available to sell to customers. The desire for control over the oxygen production process is also an issue to be considered in the decision to purchase oxygen from the market or produce it on site.

Areas deserving closer attention based on the results of the parametric studies include the maximum cycle temperature and the intercooler and condenser exit

temperature. Table 4.2 shows that a first law efficiency increase of 2.4 percent is possible if the maximum cycle temperature is increased to 1460°C (2660°F). On the other hand, a decrease in maximum cycle temperature to 1150°C (2102°F) leads to a decrease of in the first law efficiency of 2.8 percent. The fuel savings or additional power for sale are not insignificant, but the cost of the technology necessary to realize such elevated temperatures may prohibit their implementation in the MATIANT cycle.

A significant aspect of the cycle performance is the exit temperature of the intercoolers and condenser. Table 4.7 and Figure 4.3 both show that the power cycle performance is greatly improved as this temperature is decreased. As is the case with the maximum cycle temperature, there is a possible tradeoff between lower intercooler exit temperature and economic investment. A lower exit temperature may only be possible with exceedingly large and complex heat exchangers made from exotic heat transfer materials. This study also goes to show that there may be certain geographic areas where the MATIANT cycle is better suited to be constructed, as a location that does not have a cooling medium available to reach certain temperatures may not be the best site to erect a plant employing the MATIANT cycle. Also, the aforementioned study of maximum cycle pressure at various intercooler temperatures should be undertaken to optimize the performance of the MATIANT cycle.

Section 4.3. Alternative Method of Removing Water Vapor. Table 4.10 shows the performance of the MATIANT cycle when the refrigeration cycle shown in Figure 3.7 replaces the condenser at point *n* in Figure 1.10.

The table shows that cycle performance diminishes slightly when a refrigeration cycle is inserted into the process to cool the working fluid down to -11°C (12.2°F). This

Table 4.10. Employing Refrigeration to Remove Water From the MATIANT Cycle Working Fluid

	first law efficiency--HHV (%)	second law efficiency--(%)	heat rate (kJ/kWh)
base case	39.3	58.0	9154.4
Refrigeration	38.8	57.6	9283.3

is because the refrigeration process uses a compressor, which in this model has a power input of 11.6MW. The additional power requirement of this compressor is partially offset by the lower compression power requirement in the first compressor stage. Because of the lower inlet temperature to the first stage compressor, the power input to achieve the same pressure ratio is less. Refer to section 4.2.5 for the reason for this occurrence. Because of the lower inlet temperature, the power needed by the first compression stage decreases by 8.9 MW. A further reduction in compression power is observed because there is less water vapor traveling through the compressors. Most of the water vapor is removed in the phase separator following the refrigeration process rather than being removed in stages in the compression train. Because there is no water vapor to compress, the compression power is further decreased by approximately 0.5MW, leading to a net 2.1MW increase in net compression power required by the MATIANT cycle when a refrigeration process is used. Because the inlet and outlet conditions for the expanders are unaffected by the insertion of a refrigeration process, net cycle power output is decreased by this amount. This accounts for the slightly lower cycle performance. One point of consideration is that the first stage compressor may require special materials of construction due to the low inlet temperature.

When it is possible to cool the working fluid down to 30°C (86°F) in the intercoolers, the use of a refrigeration process offers a nearly identical performance option to the base case MATIANT cycle. This is advantageous to know if there is a strong desire to ensure that a minimal amount of water vapor enters the compression process. Utilizing a refrigeration process helps to minimize the concentration of the water vapor in the compressor train inlet stream. However, it is noted that refrigeration may be needed in warmer climates to ensure that enough water vapor is removed from the working fluid so that it is not present in large amounts in the sequestration stream of carbon dioxide that is split from the cycle. Therefore, the base case configuration of the MATIANT cycle, with only a condenser to remove water vapor, is compared to the refrigeration option at intercooler exit temperatures of 40, 45 and 50°C (104, 113 and 122°F). As Figure 3.7 shows, the refrigeration process incorporates precooling prior to heat exchange between the working fluid and the refrigerant. The temperature at point 2 in Figure 3.7 is adjusted accordingly to reflect what is possible given the cooling media available. Table 4.11 compares the first law efficiency for base case configuration to that of the refrigeration option for various intercooler exit temperatures.

As can be seen in Table 4.11, the first law efficiency is consistently lower when

Table 4.11. MATIANT Cycle Performance With and Without Refrigeration at Varying Intercooler Exit Temperatures

	Base case first law efficiency—HHV (%)	Refrigeration first law efficiency—HHV (%)	Percent difference (%)
Inter T=40°C	37.2	36.2	1.0
Inter T=45°C	36.2	34.8	1.4
Inter T=50°C	35.5	33.1	2.4

refrigeration is used to condense the water vapor. While this general trend is consistent with the case where the intercooler exit temperature is 30°C, it is exacerbated as the intercooler exit temperature is raised because as the intercooler exit temperature increases, the difference between the two options increases. The greatest contributor to the decrease in first law efficiency is the compressor in the refrigeration cycle. When the working fluid can be cooled down to 40°C (104°F), the power required by this compressor is 18.9MW. When the intercooler exit temperature is increased to 50°C (122°F), the power input to this compressor is 31.1MW. Because the working fluid cannot be cooled as much in the precooler in Figure 3.7, more of the cooling load is shifted to the heat exchange between the refrigerant and the working fluid. This shift portends a higher refrigerant compressor power, which leads to a lower net cycle output and a lower first law efficiency.

From a performance standpoint, it does not seem prudent to utilize a refrigeration process to remove the water vapor, especially in warmer climates where the environmental cooling medium used in the intercoolers and condenser does not allow cooling down into the neighborhood of 30°C (86°F). The best case analyzed by this study shows a small performance debit when refrigeration is used. As the intercooler exit temperature is increased, the cycle performance is reduced. In addition to the lower performance, which translates to less power to sell or more fuel to purchase and oxygen to produce or purchase, there is more equipment to purchase and maintain for the refrigeration process: one compressor, two heat exchangers and an expansion valve (or turbine). There is also the extra piping containing the refrigerant that must be maintained to avoid leaks of a potentially hazardous or environmentally unsafe substance.

Periodically, the refrigerant must be replaced and disposed or, which requires manpower and could lead to additional plant downtime. Unplanned outages due only to the refrigeration system could lower overall plant reliability, which has an adverse impact on the ability of the plant to produce power.

One reason to consider using the refrigeration cycle is to ensure that the presence of water in the sequestration process is minimized. Using a refrigeration process offers more control over the water content, as the temperature can be set such that the water is removed prior to compression. In this way, the uncertainty of the temperature of the environmental cooling medium used in the intercoolers is no longer a concern. The impact of water in the sequestration stream removed from the MATIANT cycle is not known, nor is it within the purview of this thesis. However, this point must be addressed before making final design decisions about the MATIANT cycle. If water removal is an important factor, the economics of adding the refrigeration cycle must be weighed against the cost of heat exchangers capable of supplying the interstage temperatures necessary to remove the water in the working fluid. All the while it must be kept in mind that the diminished performance of the MATIANT cycle when it contains a refrigeration process must be factored into any economic analysis.

Section 4.4. Extra Stage of Compression. Adding an extra stage of compression results in the MATIANT cycle behaving more like an ideal Ericsson cycle. Such a cycle would have a straight line between points 19 and 25 in Figure 4.1. In practice, this is the limiting case of an infinite number of compression and intercooling stages. As this is not practical, the impact of adding an extra stage of compression is to lower points 20, 22, 24 and 1 and to add another point similar to them on the bottom of the curve as well as

another point at the same temperature as 19, 21, 23 and 25. This increases the area contained in the curve. Table 4.12 compares the MATIANT cycle with five stages of compression to the base case with four stages of compression.

Table 4.12 shows that by adding an additional stage of compression, the cycle performance is improved. This is expected because there is less emergy of compression added in each stage, so the power requirements decrease. The lower compression power leads to a higher net power, as turbine inlet and outlet conditions remain unchanged. This higher net power results in the higher first and second law efficiency and lower heat rate.

Table 4.13 shows how the addition of the fifth stage of compression impacts the specific power consumed in each compressor stage. In the first three stages, the specific power decreases by at least nineteen percent. For the fourth stage, the specific power for the five stage case is actually slightly larger than that for the fourth stage case. The unique nature of the inlet conditions of the fourth stage compressor have already been discussed in section 4.2.4. The decrease is specific power is in line with expectations, as the pressure ratio in each compression stage is reduced by the addition of the fifth compressor.

Table 4.12. MATIANT Cycle Performance with Four and Five Compression Stages

	first law efficiency--HHV (%)	**second law efficiency--(%)**	**heat rate (kJ/kWh)**
base case-four compressors	39.3	58.0	9154.4
five compressors	41.0	60.5	8770.8

Table 4.13. Compressor Specific Power for Four and Five Stages of Compression

	First stage specific power (kJ/kmgol)	Second stage specific power (kJ/kgmol)	Third stage specific power (kJ/kgmol)	Fourth stage specific power (kJ/kgmol)	Fifth stage specific power (kJ/kgmol)
base case-four compressors	5018	5238	4918	3454	N/A
five compressors	4057	4015	3885	3475	2183

Adding a fifth stage of compression carries with it significant performance improvements, notably a 1.7 percent jump in first law efficiency. Adding a sixth or seventh stage would further improve cycle performance. However, economics serve to limit the number of compressors and intercoolers that can be added, as there comes a point of diminishing returns where it is not feasible to continue adding machinery. The capital costs become prohibitive and the maintenance of multiple machines becomes problematic. Furthermore, the land allocation for the plant also has finite dimensions. However, it may be advisable to consider looking at additional stages of compression if compressor discharge temperatures are deemed to be too high. More than four compression stages may also be useful when the exit temperatures from intercoolers and condensers is elevated. Having a lower compression ratio in each stage functions to counteract the effect of the higher compressor inlet temperatures, as equation 4.4 shows. As a result, in warmer climates where intercooler exit temperatures are higher, it is a valuable exercise to investigate the performance and economic benefits of adding one or more stages of compression.

Section 4.5. Comparison to a Simple Cycle. The simple cycle constructed in HYSYS is compared to the MATIANT cycle using the same parameters as above. It is mentioned in Section 2.5 and shown in Table 2.4 that the simple cycle has many of the same statepoints as the MATIANT cycle so that the comparison can be based on cycles that are as similar as possible. Figure 4.5 shows the temperature-entropy diagram for the simple cycle superimposed on the diagram for the MATIANT cycle.

Figure 4.5 clearly shows the correspondence of the temperatures at several key points in the cycles. Also, it can be seen that the general shape of the curves is similar. Table 2.4 also shows that the pressures are the same at many points in the cycle. The entropies are different due to the different working fluids in each process. Table 4.14 compares the performance of the MATIANT cycle to that of the simple cycle.

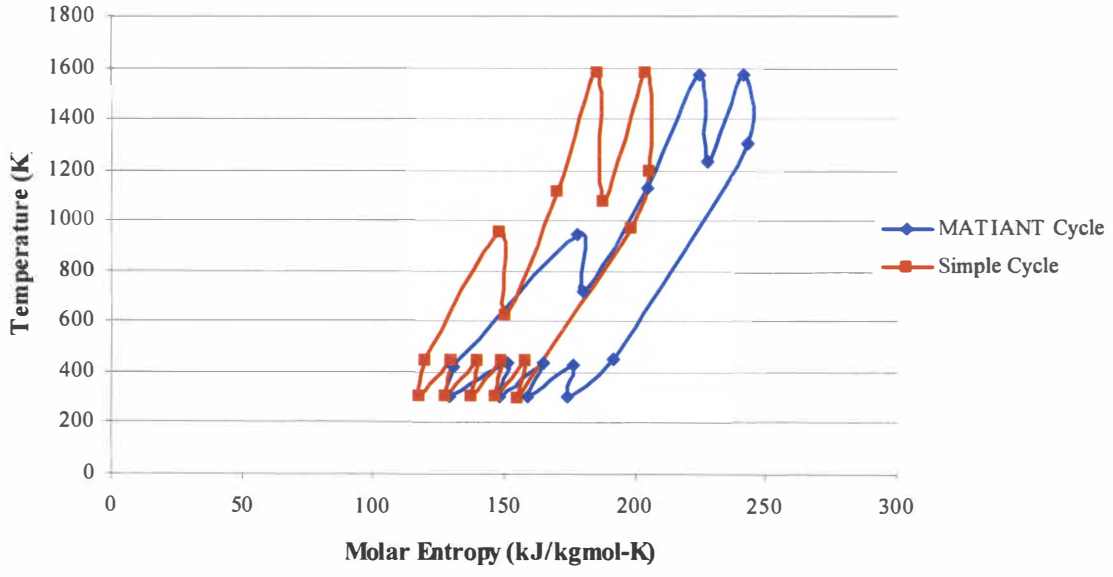

Figure 4.5. Temperature-Entropy Diagrams for the MATIANT Cycle and the Simple Cycle

Table 4.14. Performance Characteristics of the MATIANT Cycle and the Simple Cycle

	first law efficiency—HHV (%)	second law efficiency--(%)	heat rate (kJ/kWh)
MATIANT Cycle	39.3	58.0	9154.4
Simple Cycle	31.7	76.7	11348.8

Table 4.14 reveals that the performance of the MATIANT cycle is superior to that of the simple cycle on a first law efficiency and heat rate basis. However, the second law efficiency of the MATIANT cycle is significantly less than that of the simple cycle. This is especially surprising considering that the back work ratio of the MATIANT cycle is over five percent less than that of the simple cycle. The back work ratio is defined by Moran and Shapiro as the ratio of the required compressor power input to the turbine power output [68]. Table 4.15 shows these numbers for the two power cycles.

Back work ratio as defined by Moran and Shapiro only takes into account the power debit associated with the compressors. In addition to the compressors, the base case MATIANT cycle has an air separation unit that requires 53.2MW of power to produce the oxygen required by the power plant. When this is considered, the back work ratio of the MATIANT cycle becomes 50.1 percent, which is 5.4 percent less than the back work ratio of the simple cycle. Besides the air separation unit, there are other characteristics of the MATIANT cycle that reduce its net power output. Seven percent of the carbon dioxide stream is withdrawn from the cycle after it is compressed. This means that 12.5MW of the compression power input is not expanded to produce power. Put another way, the exhaust products from the MATIANT cycle are more removed from the dead state than the effluents from the simple cycle, meaning that more availability exits

Table 4.15. Compressor and Turbine Power and Back Work Ratio for the MATIANT Cycle and the Simple Cycle

	Turbine power output (MW)	Compressor power input (MW)	Back work ratio (%)
MATIANT Cycle	490.8	192.9	39.3
Simple Cycle	440.8	197.2	44.7

the MATIANT cycle than the simple cycle. This also serves to lower the second law efficiency. Section 2.4 notes that the maximum pressure in the cycles is different, even though the inlet pressure to the high pressure expander is the same in each case. This is because after exiting the compression train, the working fluid in the MATIANT cycle is warmed in a heat exchanger, which causes a two percent pressure drop. While the increase in temperature is desirable in that it enhances the power production in the turbine, there is some lost work associated with the pressure drop. The simple cycle contains no such heat exchanger upstream of the high pressure turbine. There is, however, a heat exchanger downstream of this turbine where some work is destroyed. In order to make the inlet pressure to the intermediate pressure turbine the same in both cycles, the pressure drop in the high pressure turbine of the simple cycle is less than that in the same piece of equipment in the MATIANT cycle. Therefore, the overall effect of the pressure drop in the heat exchanger of the MATIANT cycle is considerably less important than the impact of the air separation unit and the availability lost in the sequestration stream. Due to the fact that the air separation unit imposes such a large power draw on the MATIANT cycle, it is profitable to compare the simple cycle to the MATIANT cycle without an air separation unit. To do this, data is taken from Table 4.3.

The case where the oxygen delivery pressure is 689.5kPaa (100psia) with a temperature of 24°C (75°F) is compared to the simple cycle in Table 4.16.

From Table 4.16, it can be seen that the second law efficiency of the MATIANT cycle with the conditions shown approaches the second law efficiency of the simple cycle. Further improvement in the second law efficiency of the MATIANT cycle compared to the simple cycle is possible if an extra stage of compression is added or if the oxygen delivery pressure is higher. However, given that fuel is not priced on the basis of its availability (in a thermodynamic sense) but on its energy content, the inferior performance of the MATIANT cycle on a second law basis is not a matter of great concern at this point in time.

On the basis of the above analysis, it can be concluded that the MATIANT cycle is technically equal or even superior to a simple cycle process with many of the same operating conditions. By changing certain parameters in the MATIANT cycle, it can be made even more attractive on a technical basis. Examples of these improvements include adding a stage of compression, using oxygen from a pipeline or raising the maximum cycle temperature. It is important to note that the economic impact of these changes is not addressed in this thesis. Even though using oxygen from a pipeline may enhance the technical performance of the MATIANT cycle, there may not be an economic

Table 4.16. MATIANT Cycle with No Air Separation Unit Compared to Simple Cycle

	first law efficiency-- HHV (%)	**second law efficiency-- (%)**	**heat rate (kJ/kWh)**
MATIANT Cycle, O2 T=24°C, p=689.5kPaa, no ASU	47.0	69.4	7661.1
Simple Cycle	31.7	76.7	11348.8

justification to do this. It is possible that product streams from a dedicated air separation unit, such as argon, could be sold and the additional income from the sale of argon could exceed the price of the power that is consumed by the air separation unit. This is a study that is not undertaken in this thesis. However, the results of this thesis serve to provide a reason to investigate the economics of the MATIANT cycle, as it has been established that its technical performance is acceptable when compared to standard cycle already in use to generate power.

Section 4.6. Component Analysis of the MATIANT Cycle. Table 4.17 shows the irreversibility and second law efficiency of the individual components of the MATIANT cycle. For all these calculations, it is assumed that there is no heat lost to the environment from any of the unit operations. This is clearly an idealized scenario and in practice there will be some radiation and convection heat loss to the surroundings by the components of the MATIANT cycle. This means that the actual second law efficiency of each apparatus is higher than will be encountered when the MATIANT cycle is constructed. As a result, the actual irreversibility of each piece of equipment will be greater than shown in Table 4.17. Therefore, when constructing the MATIANT cycle, it is advisable to minimize heat loss to the atmosphere from all unit operations in order to achieve the highest possible efficiency and the lowest possible lost work.

Table 4.17 shows that the greatest contributors of irreversibility in the MATIANT cycle are the two combustion chambers, while the compressors destroy the largest percentage of entering availability. From this, it can be concluded that proper selection of turbomachinery is important in minimizing the destruction of availability in the MATIANT cycle. This means that machines should be chosen such that the maximum

Table 4.17. MATIANT Cycle Individual Component Performance

Component	Second Law Efficiency (%)	Irreversibility (MW)
Low Pressure Turbine	96.2	6.2
Intermediate Pressure Turbine	96	7.6
High Pressure Turbine	94.2	6.8
First Stage Compressor	83.6	8.5
Second Stage Compressor	82.8	8.9
Third Stage Compressor	85.3	8.2
Fourth Stage Compressor	84.9	5.8
Central Heat Exchanger	92.1	25.4
First Intercooler	--	11
Second Intercooler	--	11.9
Third Intercooler	--	15.3
Condenser	--	16.4
Splitter	--	8.6
Phase Separators (4)	--	0.01
First Combustion Chamber	86.9	86
Second Combustion Chamber	88.4	73

polytropic efficiency occurs at the specified operating point in the MATIANT cycle. Another point of interest from the table centers about the carbon dioxide stream that is removed from the process for sequestration. Recalling the discussion about lost availability in the exhaust stream of the MATIANT cycle, it can be observed from Table 4.17 that 8.6MW of availability is lost in this stream.

Focusing on the intercoolers, Table 4.17 illustrates that the intercoolers destroy 38.2 MW of availability, while an additional 16.4MW is lost in the condenser. Even though this is a significant amount of lost work, it is important to note that the purpose of the intercoolers is to reduce the compression power. As explained in Section 4.2.5, a lower exit temperature from the intercoolers and condensers means a higher cycle efficiency. Therefore, the lost work in the intercoolers and condenser is accepted due to

the benefit that they bring in lowering compression power. However, careful attention should be given to this area in detailed design and optimization of the MATIANT cycle performance to ensure that the compression power saved is not exceeded by the availability destroyed in the cooling process.

Section 4.7. Conclusions and Recommendations for Further Study. Section 1.6 of this thesis states that it is important to know that the MATIANT cycle is theoretically feasible and to ascertain how it compares to a standard power plant that uses natural gas. In theory, the MATIANT cycle offers an attractive alternative to generating power while mitigating harmful emissions to the atmosphere: it uses a well established fossil fuel in natural gas and employs mostly proven equipment while eliminating nitrous oxide and carbon dioxide from the exhaust stream. It accomplishes these two goals by combusting natural gas in pure oxygen from an air separation unit (thereby eliminating nitrous oxides) and allowing for carbon dioxide to be split from the working fluid in a controlled manner for sequestration by any number of methods (thus getting rid of carbon dioxide emissions). While sounding appealing, the MATIANT cycle must be proven to be a worthy successor to the conventional fossil fuel power plants. It must be found to be technically and economically sound in comparison to these traditional methods of power generation to progress from dream to reality. This thesis seeks to confirm the technical viability of the MATIANT cycle as well as understand the impact of various parameters on its performance. The technical viability is verified by comparing it to a simple cycle that combusts natural gas in air. To provide a better assessment, many of the key statepoints in the simple cycle are modeled to be the same as those found in the MATIANT cycle. The result of this examination is that the performance of the

MATIANT cycle is equal or even better than that of the simple cycle. The heat rate of the MATIANT cycle is nineteen percent lower than that of the simple cycle. This translates into lower fuel usage and therefore operating costs for the MATIANT cycle. Along the same lines, the first law efficiency of the MATIANT cycle is 7.6 percent greater than the first law efficiency of the simple cycle. It is not insignificant that the MATIANT cycle model employs only four compressors, while the simple cycle needs thirteen total compressors to reach the same key statepoint values as the MATIANT cycle, summarized in Table 2.4. More pieces of machinery means that there are more unit operations that can fail as well as higher operation and maintenance costs.

Looking to the MATIANT cycle itself, it can be seen that the most important cycle parameters are intercooler exit temperature and maximum cycle temperature. Table 4.7 shows that the first law efficiency of the MATIANT cycle increases by almost four percent when the intercooler exit temperature is decreased from 50°C (122°F) to 30°C (86°F). If the maximum cycle temperature can be increased from 1300°C (2372°F) to 1460°C (2660°F), the first law efficiency can be increased from 39.3 percent to 41.7 percent. Another cycle modification is to add one more stage of compression. At the same maximum cycle pressure as the base case, the first law efficiency increases by 1.6 percent.

Having established that the MATIANT cycle is both technically sound and technically preferable to a simple cycle, the next step is to determine if the MATIANT cycle is both economically sound and economically preferable to the simple cycle. It has been a common theme throughout this thesis that economics is not part of this initial study. However, economics plays an integral role in the final acceptance or rejection of

the MATIANT cycle as a method of producing electricity. It is therefore recommended that the next step in the qualification process of the MATIANT cycle be a detailed economic analysis. Not only will this study focus on the capital expenditures associated with the construction of the MATIANT cycle, but it will also deal with the operating expenses. Ultimately, the goal is to ascertain if power from the MATIANT cycle is economically competitive with power from a conventional process and whether the rate of return of the MATIANT cycle is comparable to that of a traditional power plant. If the answer to both of these questions is "yes," then the MATIANT cycle will be certified as a feasible alternative to conventional power plants with the advantage of mitigating the emission of anthropogenic carbon dioxide to the atmosphere.

Not only must the MATIANT cycle be compared to a simple cycle on the basis of economics, but the various configurations of the MATIANT cycle explored in this thesis must be compared to one another. For instance, it is known that adding a stage of compression enhances the performance of the MATIANT cycle, but it must be determined if this is an economically wise configuration. Furthermore, increasing the maximum cycle temperature increases the efficiency of the process. However the development of the technology to realize these temperatures in practice may be cost prohibitive.

The source of the pure oxygen required by the MATIANT cycle will also come down to economics. The base case receives oxygen from an air separation unit dedicated to the MATIANT cycle. While this allows for the power plant to avoid sharing the air separation unit with other users, it also requires the plant to take a performance hit in that it must supply (or pay for) the power required by the air separation unit. The use of a

dedicated air separation unit requires 53.2MW to be debited to the MATIANT cycle. When oxygen is received from a pipeline, the first law efficiency can be increased by almost eight percent and the heat rate can be lowered by over sixteen percent. This translates into lower fuel costs. On the other hand, it is possible that the air separation unit could be used to produce argon, which could be sold on the market for additional revenue. Furthermore, receiving oxygen from a pipeline dictates the need for oxygen compressors. The presence of pure oxygen near the lubricating oil of the compressor presents a potential safety problem that must be considered in the final analysis.

It is also worth noting that the air separation unit design described in the Appendix of this thesis is realistic, but not necessarily optimized. While approved as feasible by industry, it is not designed by experts in the area of cryogenics and air separation. Therefore, it is a worthwhile exercise to investigate the optimization of the air separation unit, which could lower the power requirements.

Although sequestration is not directly considered in this study, the economics associated with the sequestration of carbon dioxide must also be accounted for in the cost analysis of the MATIANT cycle. Chapter 1 lays out several sequestration methods where study is ongoing. Once a feasible method is identified for sequestering the carbon dioxide stream taken from the process, the cost of it must be analyzed and incorporated into the economic analysis of the MATIANT cycle. In addition, there is an energy penalty associated with the sequestration of the carbon dioxide. It is also important to note that the decision to build the MATIANT cycle cannot be made without an approved method of sequestering the carbon dioxide.

The model of the MATIANT cycle analyzed here assumes that it is possible for the turbine inlet to reach 1300°C (2372°F) or higher. In practice temperatures of this magnitude pose major metallurgical problems and are certainly not possible without cooling the turbine blades. Greater focus on the expanders is therefore recommended, as research in that area will increase the inlet temperatures that can be realized. Also, a study of the method for cooling of the turbine will give a more complete picture of cycle performance and perhaps provide a way to reach the temperatures modeled in this thesis.

A final recommendation for further study is the concept of a power plant that allows for carbon dioxide capture. The MATIANT cycle is just one of many methods that could be employed to mitigate carbon dioxide emissions to the atmosphere. Continued effort should be given to the development and analysis of power cycles that use conventional sources of fuel but allow for capture of carbon dioxide.

In conclusion, the technical validity of the MATIANT cycle has been well established, although there are opportunities to boost its attractiveness by making adjustments in statepoint values or the cycle configuration. Determination of the economic feasibility of the base case cycle and the various alternatives is the next step in the qualifying the MATIANT cycle as a legitimate means of generating power that does not contribute to the harm of the environment.

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APPENDIX

Air Separation Unit

Section A.1. Preliminary Considerations. The MATIANT cycle is a semi closed power plant designed to reduce carbon dioxide and nitrous oxide emissions to the atmosphere while continuing to use proven methods of producing power. Natural gas is combusted in pure oxygen to produce carbon dioxide and water. Because pure oxygen is the oxidizer in the combustion process, no nitrogen is present to form nitrous oxides. Heat is removed from the cycle such that the water is condensed and then removed from the process in phase separators. Once the working fluid is mostly pure carbon dioxide, a portion of the carbon dioxide is removed from the process for sequestration by an appropriate method. This sequestration prevents the emission of carbon dioxide in the exhaust stream(s) of the MAITANT cycle. The procedure to sequester the carbon dioxide is outside the scope of this thesis. The remaining carbon dioxide is recycled to expanders and combustion chambers for reheat and further expansion. Because a portion of the process stream is removed, the MATIANT cycle is considered a semi closed cycle rather than a closed cycle. The stream is removed in a controlled manner and not vented to the atmosphere without regard for its final destination, further defining the MATIANT cycle as a semi closed cycle [1]. Figure 1.10 in the main body of the thesis is a diagram of the MATIANT cycle showing in pictorial form the description above. The same diagram is shown on the following page in Figure A.1.

Two sources of pure oxygen for the combustion process are possible. One is a pipeline transporting the oxidizer from an air separation unit serving a large number of plants utilizing oxygen, while the construction and use of an air separation unit dedicated to the power plant under consideration is the other. The advantages of supplying the

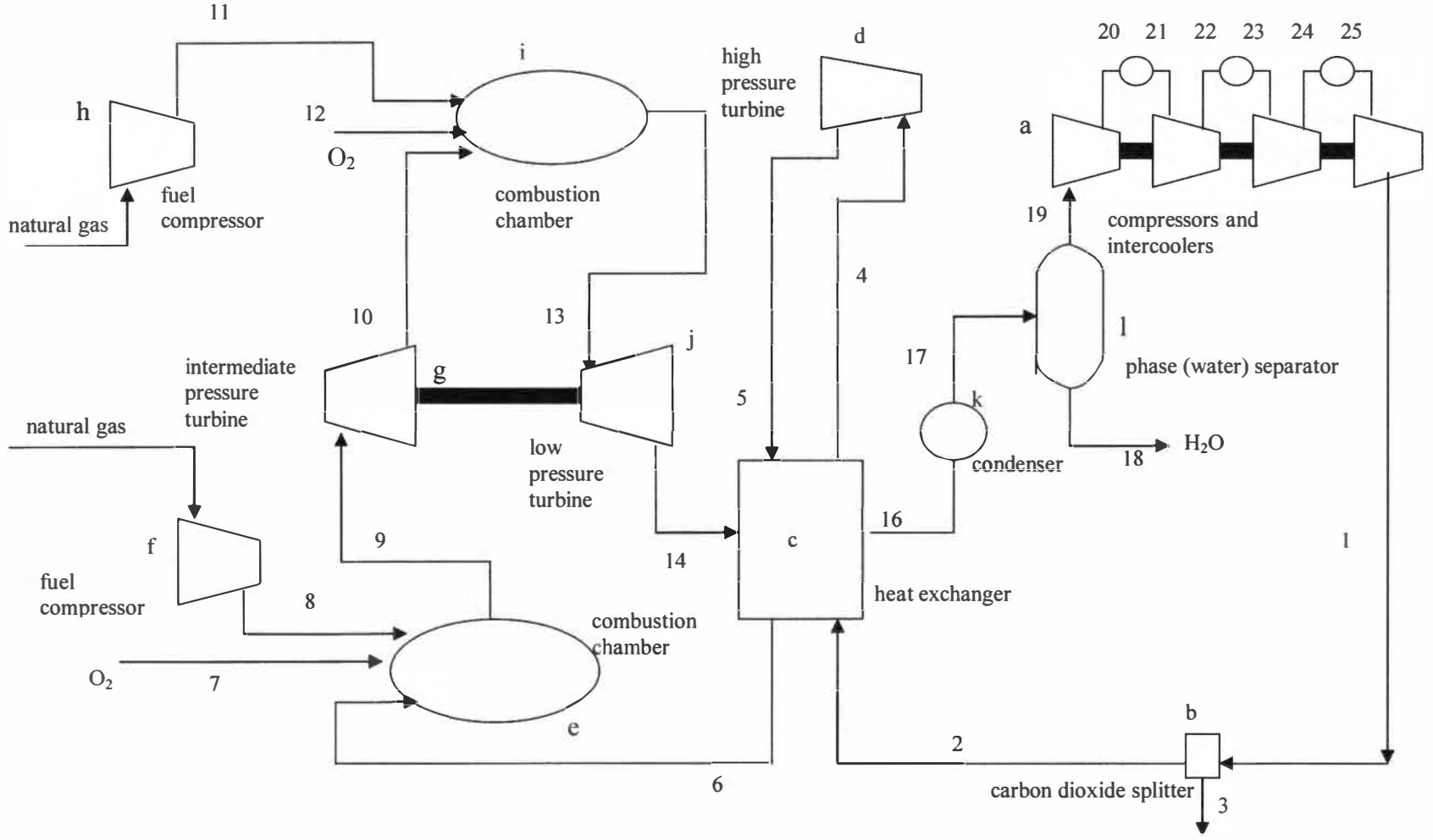

Figure A.1. Process Flow Diagram of the MATIANT Cycle

oxygen by a pipeline are no initial capital investment in an air separation unit and no concerns about the maintenance and upkeep of such a plant. In addition, power from the MATIANT cycle is not needed to power the air separation unit. On the other hand, not having a dedicated plant means that there will be an annual operating charge for oxygen use and that the power plant may not have priority in the use of oxygen produced by the source air separation unit if there is a problem at that facility. A long term contract for oxygen supply may not be as desirable as having ownership of an air separation unit whose sole customer is the MATIANT cycle. Having control over the amount of oxygen produced by the plant could be preferable, as if the MATIANT cycle is not required to produce as much power, then the production from the air separation unit could be easily turned down. However, if a contract has been entered into, then the MATIANT cycle could be locked into paying for a certain amount of oxygen, whether or not that oxygen is actually required by the power plant. Furthermore, a dedicated air separation unit could become a source of revenue for the MATIANT cycle, as the byproducts nitrogen and argon could be sold rather than being waste streams.

The decision as to which direction to take involves both economics and technical considerations. As a complete economic analysis is not a part of this study, no final decision can be arrived at in this paper. However, the performance differences between oxygen supply and oxygen production can be noted and recommendations directing further study can be made. The base case MATIANT cycle assumes that a dedicated air separation unit is employed [2]. This is primarily because of the large amount of oxygen required by the MATIANT cycle: almost 4260 tons per day for a 250MW power plant.

The Electric Power Research Institute (EPRI) notes in its Report AP-3499 that "...the cryogenic process is most economical method for large scale oxygen production...[3]"

In spite of this, a sensitivity is included in the body of the thesis that highlights the technical differences between the two options. Because the base case model has a dedicated air separation unit, a model of such a plant was constructed in HYSYS to determine the power that must be drawn from the MATIANT cycle to power the air separation unit. This power debit is included in the efficiency calculations for the MATIANT cycle. Constructing the HYSYS model also proves that an air separation unit to meet the oxygen demands of the MATIANT cycle is technically possible.

It is assumed for this project that the MATIANT cycle requires oxygen with a purity greater than 99.5 percent to mitigate the effects of inert units in the combustion process and in the sequestration process. This assumption will be more fully developed in a later section of this Appendix. Also for this project, the MATIANT cycle is to be a net 250MW power plant after subtracting out power needed to drive the compression process and the air separation unit. Such a power plant requires 4260 tons per day of oxygen to be supplied to the MATIANT cycle, assuming that the power plant is always running at base load. This chapter will briefly lay out the basics of the process for separating air into its constituents and then proceed to describe the method chosen to produce pure oxygen for the MATIANT cycle.

Section A.2. Summary of the Air Separation Process. McGuinness and Kleinberg [4] note six basic steps are involved in the air separation process. Atmospheric air is compressed in a train of compression and intercooling and then impurities such as carbon dioxide, methane and water are removed in one of several pretreatment processes.

The clean air stream then enters a heat exchanger where it is cooled down to the cryogenic temperatures necessary for the separation of air to occur. Cryogenic air proceeds to the distillation columns where the three main components of air, oxygen, nitrogen and argon are separated from each other. While this is happening, refrigeration is occurring in the process to maintain the cold temperatures in the coldbox where the separation takes place. The coldbox is an insulated box containing where cryogenic temperatures are experienced in the process. The coldbox contains the separation and cooling processes. If products are compressed to their desired pressure by pumping rather than compression, cryogenic pumps are also in the coldbox. Once the components of air have been separated, the products are compressed to the required pressure, which can take place before or after the products exiting the coldbox are used to cool the incoming compressed air. The difference will be discussed later when the air separation unit modeled for the MATIANT cycle is described. Figure A.2 below, based on information from the Air Products and Chemicals website [5], shows the steps in the air separation process.

Air enters the air separation unit through a series of centrifugal compressors with stages of intercooling. Within the compression train, the pressure of air is increased from atmospheric pressure to between 550 and 700kPaa (79.8 and 101.5psia). After intercooling, water can be removed from the process by means of a phase separator or coalescing filter. It is important to remove water and other components of air with high freezing points relative to the cryogenic freezing points of oxygen or nitrogen because they will be condensed or solidified in the process and cause blockages in the system.

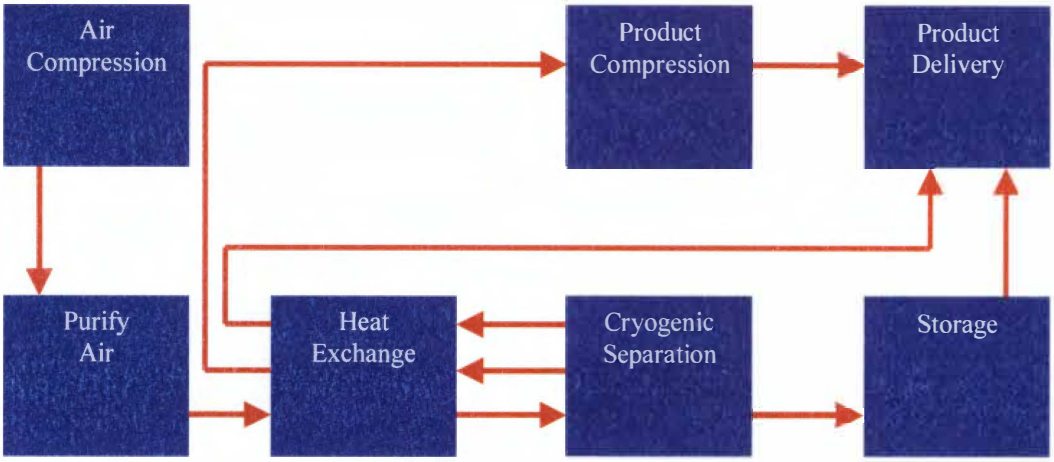

Figure A.2. Diagram of the Air Separation Process

The major importance of the compression of the air is to serve all the functional requirements of the air separation process such as reboil, reflux and air cleaning. Pressure changes can be used to match the boiling points of oxygen and nitrogen such that when oxygen is being vaporized in the separation process, nitrogen is being condensed. This point will be described later when the separation of the air into its three main components is under investigation. Special considerations in the compression process include maintaining the compressor seals and the avoidance of compressor surge. Compressor seals are operated to ensure that lubricating oil does not enter the process and become mixed into what will become an oxygen rich environment downstream of the compressors, causing a safety hazard [6]. Industry standards normally employ three stages of compression with intercooling with each compressor stage operating at a pressure ratio of 1.8 to 1.9. The compression process is the highest power consumer of the entire air separation process and also the largest contributor to cycle inefficiency, as Thorogood states that 31 percent of the total inefficiency in the air separation plant is due

to the compression train [7]. Figure A.3 below shows the compression configuration of an air separation unit.

As has been already mentioned, air contains impurities such as water, carbon dioxide, and methane. Due to their high freezing points, these constituents of air solidify at the cryogenic temperatures present in the air separation process and cause blockages in the system. Furthermore, the trace amounts of hydrocarbons in air can present a combustion hazard in the oxygen rich environment of an air separation unit. Thorogood explains the three processes have been used to provide the necessary purification of the compressed air. Two of them, regenerators and reversing heat exchangers, involve the simultaneous cooling and purification of the air. Figure A.4 shows the arrangement used to purify and cool the air at the same time.

As the figure shows, the cold products of the separation process are used to cool the incoming high pressure air. The feed air, containing the impurities present in the

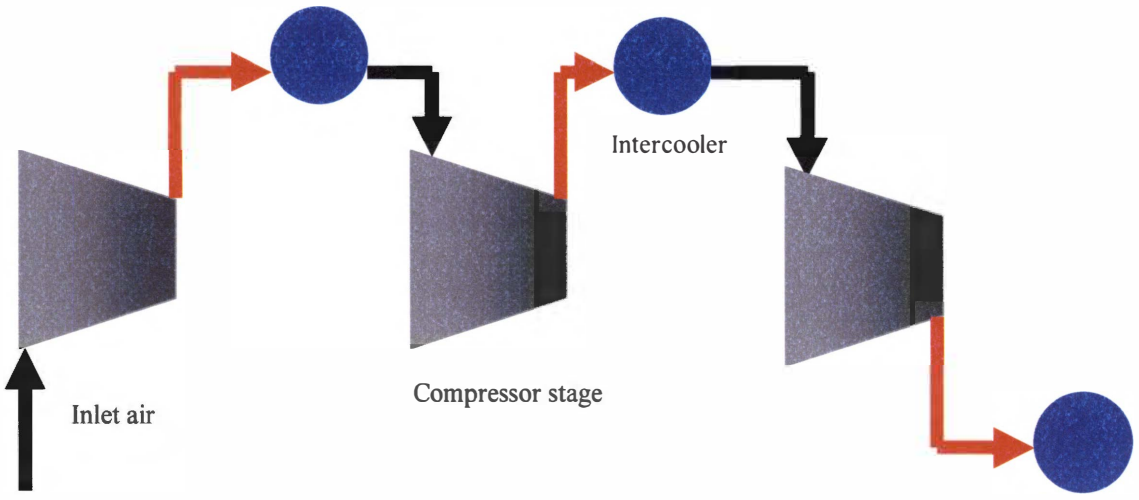

Figure A.3. Typical Compression Train in an Air Separation Unit

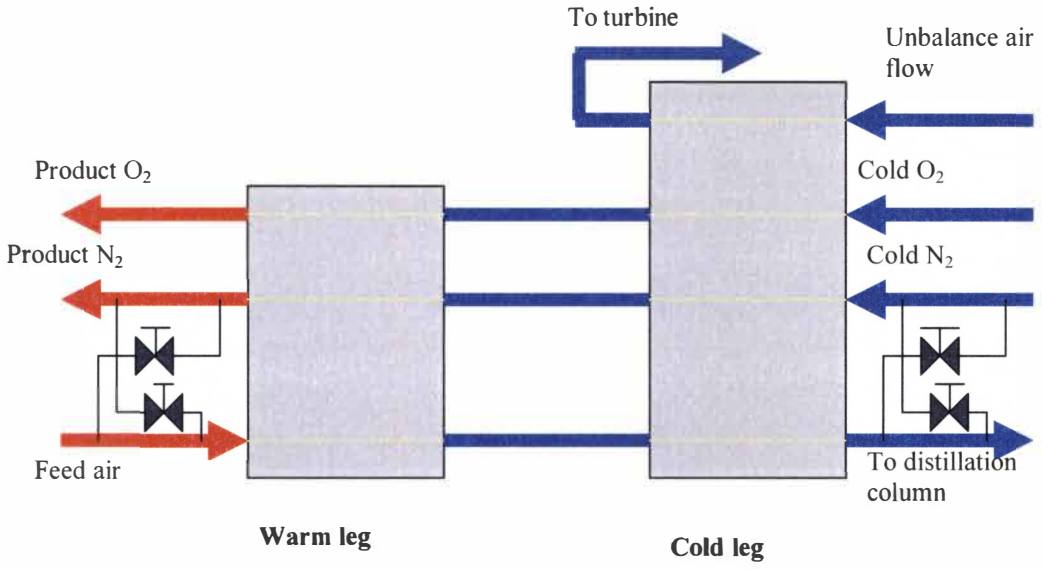

Figure A.4. Air Treatment with Simultaneous Cooling and Purification

atmosphere, enters the warm leg of the heat exchanger where it is cooled down to the cryogenic temperatures of the cold nitrogen and oxygen exiting the separation process. The unbalance air flow shown passing through the cold leg will be described later. As the air is cooled, the impurities with high boiling points condense or solidify along the walls of the heat exchanger channel. When it has been determined that the channels need to be cleaned of the removed impurities, the nitrogen and air flows switch channels, as indicated by the presence of valves on each of these channels. The air now flows through the clean nitrogen channel while the nitrogen flows through the channel that air had been flowing through. The warm nitrogen vaporizes the liquid or solids in the channel and carries them out of the system. This cyclical process is repeated as necessary during the operation of the process. While serving the purposes of removing impurities in the air and cooling it to cryogenic temperatures, these processes result in a 1-2 percent loss of air during the switching of the flows. This is an unwanted impact, as the loss of air portends

the loss of power that can be conserved in the cycle. Furthermore, the impurities actually enter the coldbox of the air separation unit.

In an effort to combat the loss of air found in the simultaneous cooling and purification process and to eliminate the impurities prior to their entrance into the coldbox, current practice separates these steps. To clean the air of impurities, molecular sieves using the adsorption process are employed.

Molecular sieves are capable of cleaning the air using pressure swing adsorption or temperature swing adsorption. In either of these processes, two chambers are used, each filled with a bed of pebbles. Before entering the molecular sieves, the air is precooled to near the freezing point of water to minimize the water load and maximize the removal of carbon dioxide in the molecular sieves. As the air passes through the bed of pebbles, the unwanted contaminants are adsorbed onto the bed of pebbles. When the pebbles are saturated with impurities, the air stream is switched to the other molecular sieve while a waste stream passes through the saturated bed. The pressure is decreased and the impurities are released or the temperature is increased and the impurities are released. The former process is pressure swing adsorption, while the latter process is temperature swing adsorption. In either case, the impurities are transported from the cycle by the outgoing nitrogen stream. For temperature swing adsorption, the cycle is four to six hours, while for pressure swing adsorption the cycle time is four to eight minutes. Figure A.5 is a diagram depicting the temperature swing adsorption process without cooling using molecular sieves. Molecular sieves cause a five to seven percent pressure drop in the feed air stream, but allow for the coldbox to be simpler because the impurities are removed from the process prior to the stream entering the coldbox [8]. The

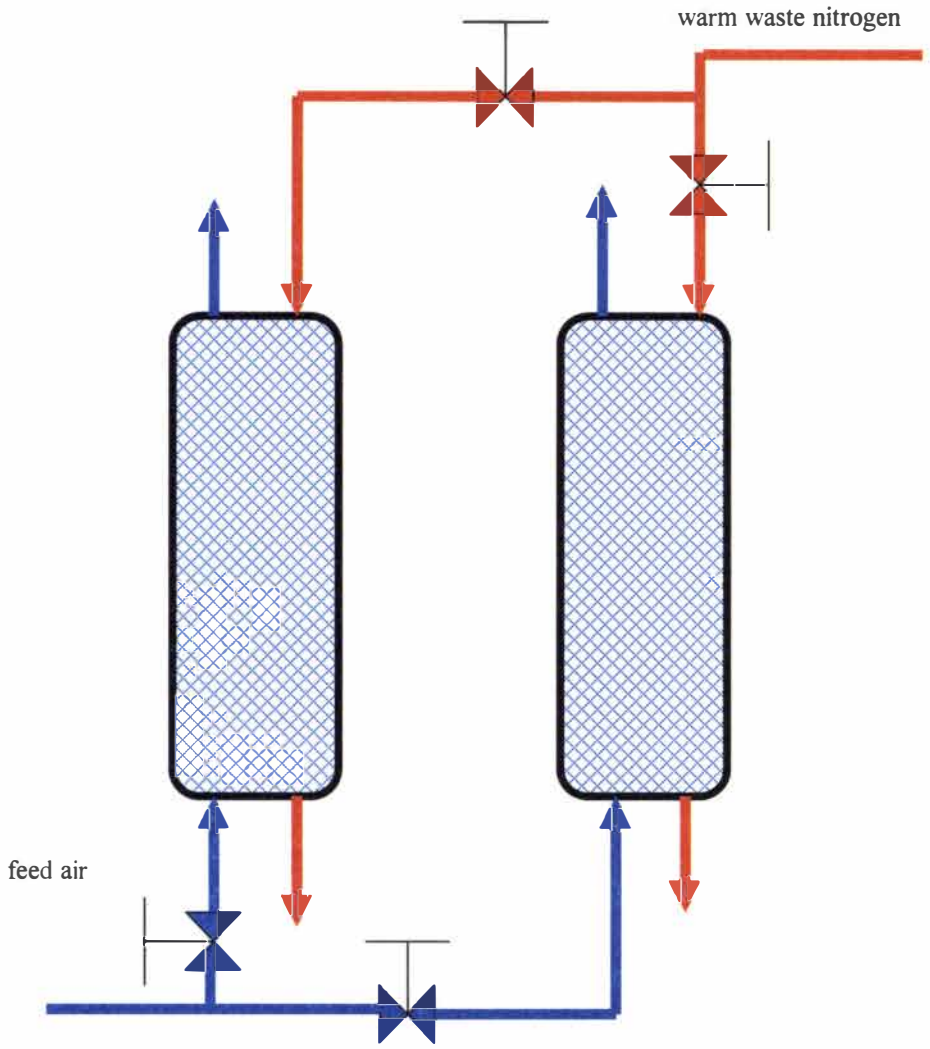

Figure A.5. Purification of the Air Using Molecular Sieves

maximum diameter of the beds is fourteen feet due to shipping concerns, as found in McGuinness and Kleinberg [9]. However, industry representatives state that there is not a set limit on the height of the bed, so they can be made as long as possible to ensure that only two beds are employed: one cleaning the air and one being regenerated.

After being cleaned, the air enters the coldbox through the main heat exchanger. The main heat exchanger cools the incoming air to cryogenic temperatures against the outgoing cold products. Not only is the incoming air cooled, but the outgoing products are heated and vaporized as necessary. As described by Barron, this serves to "conserve cold" in the process by using exergy in the cold streams to cool the incoming warm streams [10]. According to McGuinness and Kleinberg, the main heat exchanger is a multichannel, counterflow brazed aluminum plate fin heat exchanger [11].

Air enters the separation portion of the air separation unit as a clean, cold stream. The composition of the air is nitrogen, oxygen and argon with trace amounts of other Noble gases. Separation of the air into its main components is accomplished by a double distillation column. Normal distillation processes involves only a single column as shown in Figure A.6.

King describes distillation as a process in which a mixture is separated by means of a difference in the partial pressures of the components of that mixture. Vapor travels up the column while liquid travels down the column. The more volatile, lower boiling point component, is produced as the overhead vapor project while the less volatile, higher boiling point component, is a bottom liquid vapor. The highest pressure in the distillation process is observed in the reboiler where the liquid product is vaporized and then travels up the column due to a pressure drop up the length of the column. The

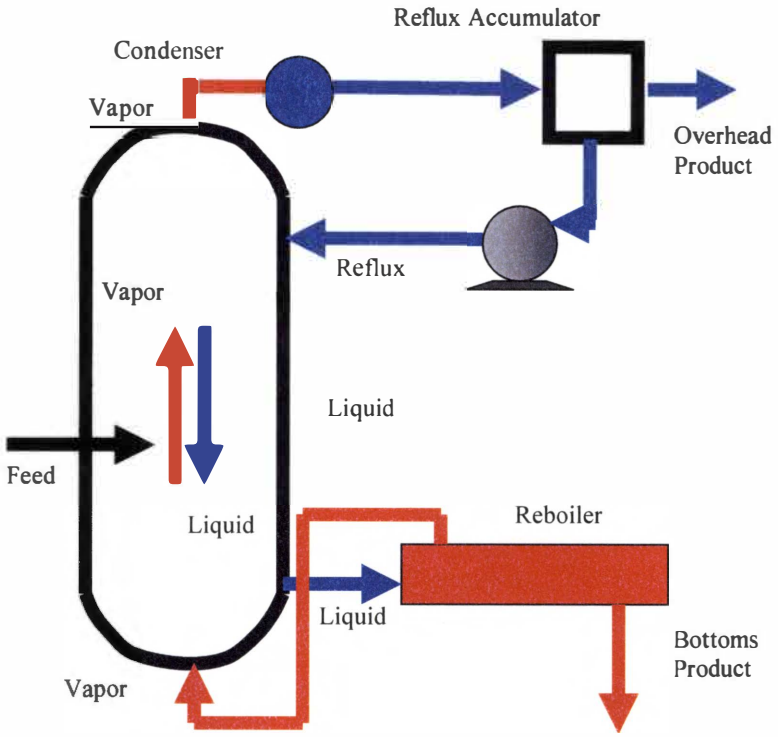

Figure A.6. Diagram of a Typical Distillation Process

lowest pressure occurs in the condenser, where a portion of the overhead vapor product is condensed and sent back to the distillation column as reflux. The reflux serves to strip the heavier components from the rising vapor. Above the feed point is the rectifying or enrichment section of the column, where the heavier components are removed from the upward flowing vapor. The stripping section is below the feed point where the lighter component is stripped from the downflowing liquid [12].

While the air separation process uses two distillation columns rather than one because, as Barron informs, too much oxygen escapes in a single column process, the principles are the same. The two columns are thermally linked by means of a condenser-reboiler. This piece of equipment serves as a condenser for the overhead product from the lower column and a reboiler for the upper column. The lower column is a high

pressure column fed by air high pressure, cold, clean air that produces highly pure nitrogen as a vapor product and enriched oxygen as a liquid product. Some nitrogen is refluxed into the high pressure column. This column is similar to a rectifying section of a single distillation column. The upper column is a low pressure column is fed by the enriched oxygen from the high pressure column and has some of the liquefied nitrogen from the condenser-reboiler as reflux. The products of the low pressure column are highly pure oxygen as the bottoms products and highly pure nitrogen as the overhead product [13]. An option in an air separation unit is an argon rich vapor sidestream that can be sent to another column to produce pure argon. Argon separation will be detailed later in this chapter. Comparing this to a single distillation column, the low pressure column is tantamount to a stripping section.

The columns are operated at different pressures to allow for the condenser-reboiler to function, as described by industry representatives. While the high pressure column has a maximum pressure of over 600kPaa (87psia), the low pressure column has a maximum pressure of 170kPaa (24.7psia). The difference in pressures between the columns causes the boiling point of nitrogen to be greater than that of oxygen. Normally, nitrogen has a lower boiling point than oxygen. However, because nitrogen is at a higher pressure than normal, its boiling point increases. The pressures of the columns are controlled such that the boiling point of nitrogen is indeed greater than that of oxygen. Because of this, heat is transferred from the nitrogen vapor to the oxygen, condensing the nitrogen and vaporizing the oxygen. The oxygen vapor now rises up the low pressure column while the liquid nitrogen is refluxed to the high pressure column and, after a

pressure decrease, refluxed to the lower column as well [14]. Figure A.7 shows the double column arrangement for an air separation unit.

In spite of the best efforts of air separation unit designers and builders to ensure that there is no loss of energy from the process to the surroundings, there are nonetheless some losses from the air separation unit. The three main sources of losses in the process, as quoted by McGuinness and Kleinberg, are heat leak into the coldbox, warm end losses in the main heat exchanger and the production of liquid products. To counteract these losses, refrigeration is required. This refrigeration is supplied by one of two methods: Joule-Thomson expansion or expansion in a gas turbine. Expansion in a gas turbine is preferred because this can serve as a source of additional power production, thereby

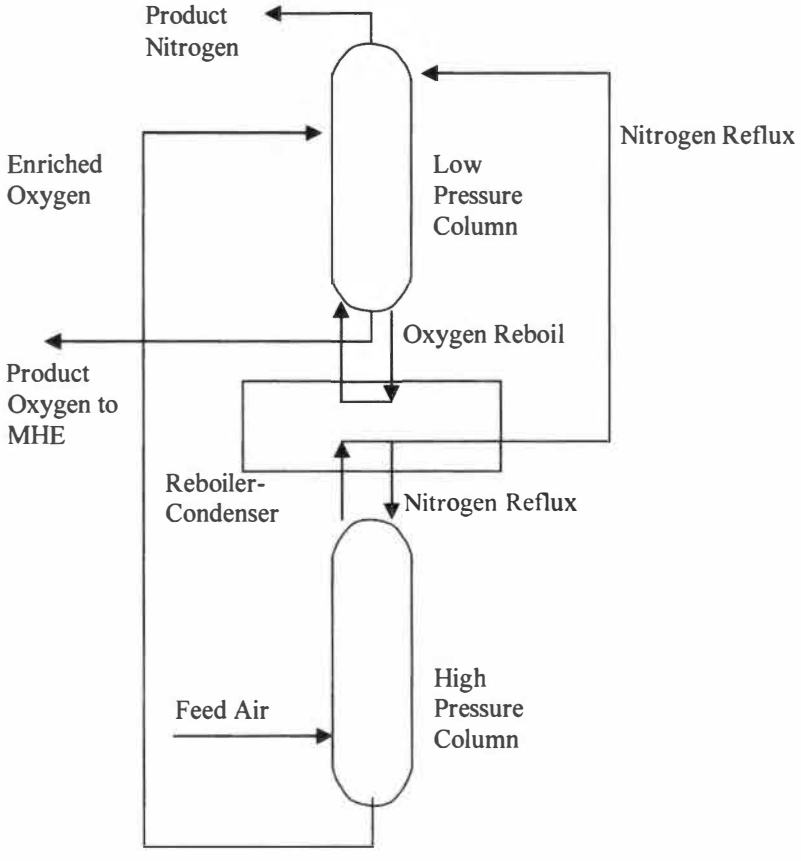

Figure A.7. Typical Double Column Arrangement for an Air Separation Unit

mitigating the power demands of the air separation unit. Also, a certain pressure drop in a turbine produces a much larger temperature drop than the same pressure drop in a throttling process. Consequently, the pressure does not have to be dropped as much to achieve a certain amount of refrigeration. The amount of refrigeration required to balance the losses can have an impact on the purity of the oxygen or argon streams because less air is input into the high pressure distillation column, but this concern can be handled by properly designing the overall process [15].

After air has been separated into its constituents, the components are ready to leave the coldbox as products. At the exit from the double distillation column, the oxygen and nitrogen are both slightly above atmospheric pressure. The desired pressure of the products may be significantly higher, as is the case for the oxygen for the MATIANT cycle. In this application, the oxygen must be delivered at 3500kPaa (508psia) and 500kPaa (72.5psia). Therefore, compression of the products exiting the distillation process is the next step in the air separation process. If the oxygen passes through the main heat exchanger to cool the incoming air prior to being compressed, it undergoes compression as a vapor in oxygen compressors. McGuinness and Kleinberg note that the oxygen compressors can be centrifugal or reciprocating depending on the volumetric flow in the final compressor stage. Whichever type of compressor is utilized, care must be taken due to the safety hazards present in oxygen compression. Most notable among the safety concerns is the potential for an explosion should the oxygen and compressor lube oil mix. The oxygen rich environment present in the oxygen compressors is conducive to such an event [16].

A United States Patent summary describes an alternative to compressing oxygen as a vapor is to pump the nearly pure liquid bottoms product to its delivery pressure prior to using it to cool the incoming feed air. Such an arrangement is called a pumped liquid oxygen (pumped LOX) cycle [17]. Industry representatives confirm in a personal communication that this application has been finding more and more favor in air separation unit design. Although safety concerns are driving the shift, there is the added benefit of lowering the overall work requirements of the air separation unit because pumping a liquid to a certain pressure requires less work than compressing a vapor of the same composition to the same pressure.

Although the benefits of pumping oxygen to the pressure required by the end user are obvious, there are some drawbacks to the pumped LOX process. Foremost among these is that liquid is being removed from the distillation column, a process noted earlier to be a source of refrigeration losses for the air separation unit. The refrigeration to balance this loss comes in the form of condensed air input into the double distillation column. Condensing the air requires some additional compression power, partially offsetting the gain in power that stems from pumping the oxygen rather than compressing it. Furthermore, this compressed air stream must be passed through the main heat exchanger, complicating the design of this piece of equipment. This accounts for the "unbalance air flow" stream shown in Figure A.4, the reversing heat exchanger diagram. For each liquid oxygen process stream, there must be a condensed air stream, meaning that the air separation unit for the MATIANT cycle would require two condensed air streams input into the double distillation column. For each mole of oxygen produced at a certain pressure, 1.4 moles of air at a pressure 150-250 percent of the oxygen pressure is

required. This is due to the differences in the boiling points and latent heat of the two streams. As was mentioned previously, the production of liquid products can negatively impact the purity of the oxygen and argon streams if the design is not done correctly. The disadvantages associated with pumped LOX cycles are normally accepted due to the increased safety of the process versus a gaseous oxygen process [18]. Figure A.8 shows a pumped LOX cycle. The only difference between this figure and Figure A.7 is the oxygen pump, which is darkened in Figure A.8 to highlight its addition.

Barron describes a final part of many air separation units is the argon recovery column. By volume, normal air has about 0.9 percent argon, 1.23 percent by mass. Current technology allows for 90 percent of this to be recovered, mostly for use in MIG welding or incandescent lamps. To achieve this, a vapor sidestream containing 12 to 15 percent argon by volume and no nitrogen is withdrawn from the low pressure distillation column. This stream is introduced into an argon rectifying column, where argon is the overhead vapor product and oxygen is the liquid bottoms product. The oxygen is recycled to the low pressure distillation column [19]. Industry experts note that this process is possible only for an air separation unit producing oxygen with a purity greater than 96 percent. Recovering argon as a liquid can adversely affect oxygen purity, meaning that allowances must be made to balance the refrigeration losses attendant to removing the argon rich stream from the process. Assuming that there is a market for the argon produced by the air separation unit, namely a strong manufacturing sector, this option alone can make the air separation unit profitable and speed up the recovery of capital invested. However, the lack of a market to sell the argon means that the incremental investment to add the argon rectifying column is not justified, as there is no

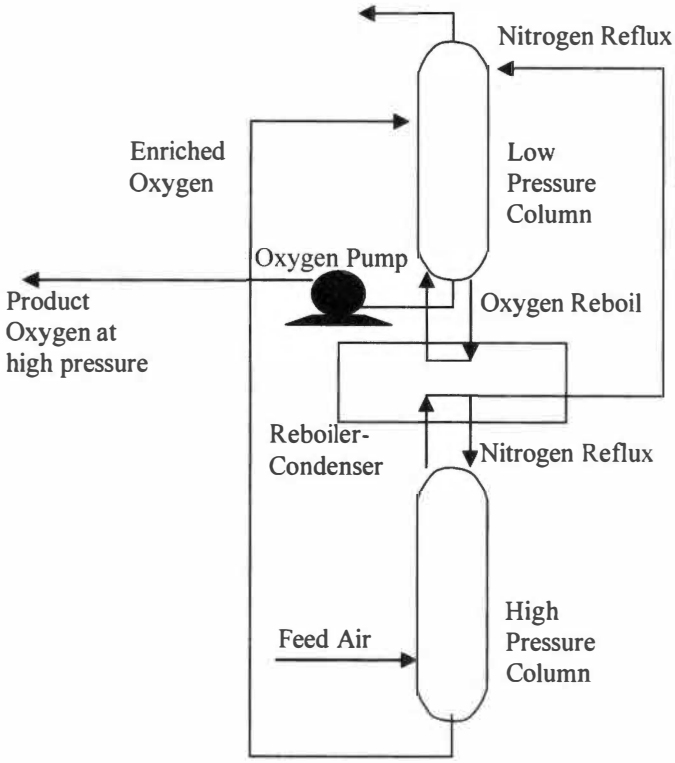

Figure A.8. Pumped LOX Schematic

way to dispose of the argon produced by the process [20].

Section A.3. Description of Air Separation Unit Modeled for Integration with the MATIANT Cycle. Based on the HYSYS simulation run for the MATIANT cycle, approximately 4260 tons per day of oxygen is required if the plant runs constantly at base load. As the opening to this chapter mentions, there are several factors to consider as to whether the oxygen should be supplied by a dedicated air separation unit is appropriate or taken from a pipeline. Because the MATIANT cycle as proposed includes a dedicated air separation unit and because EPRI notes that large oxygen customers should use the cryogenic process to meet their needs, the MATIANT cycle base case considered for this thesis includes a dedicated air separation unit. Table A.1 displays the main

Table A.1. Summary of Air Separation Unit Characteristics

Characteristic	Description	Comment
Oxygen Purity	99.78 %	Represents recovery of 99.9% of oxygen in feed air. Purity of 99.8% is normal according to industry experts and purity above 99.95% requires special processes.
Argon Recovery	73.3% at 99.9% purity	Noted by industry experts as being suboptimal (90% recovery obtainable, 80% expected) but still represents a revenue stream of $20.6 million if sold at current price. Use of pumped LOX cycle may play a factor in lower recovery.
Total Power	53.2MW	Represents just over 21% of work taken from MATIANT cycle to run processes associated with it, primarily compressors. Articles by Mathieu suggest that ASU should take 20% of work with another 6% consumed by oxygen compressors (not used in pumped LOX cycle). Without ASU, the back work ratio of the MATIANT cycle is 39%; including the ASU, it is 50%.
Main Air Compressor Power	44.2MW	For the 4259tpd plant modeled, this represents a 10.4kW/tpd; 10-12kW/tpd is considered acceptable.
Nitrogen Recovery	18,800 kgmol/hr of 99.7% pure nitrogen leaves main heat exchanger at a temperature of -18°C (-0.4°F) and a pressure of 120kPaa (17.4psia)	Several uses for this within process: cooling of molecular sieves, condensing water out of MATIANT cycle, intercoolers in ASU or MATIANT cycle or running power plant with nitrogen as working fluid. It could also be sold, although price for nitrogen is low.

characteristics of the air separation unit model constructed in HYSYS, along with industry comments [21].

Industry representatives were consulted through the process of designing and modeling the air separation unit coupled to the MATIANT cycle. While willing to provide input into the design and review the model, these engineers asked that they and their company not be identified by name in this thesis. They note that some simplifying assumptions can be made in the modeling process. First, air can be taken as a three component mixture of nitrogen, oxygen and argon. Although not exact, this is a close approximation to the actual composition of air. Outside of the three aforementioned elements, the other components of air are present in the parts per million range or less. The additional elements must be taken into account in the final design of the molecular sieves, but the three component mixture is suitable for modeling purposes. Second, it is acceptable that the purification process can be shown in the HYSYS model as a pressure and temperature drop without modeling the process that takes place inside of them. The model incorporates a cooler with a pressure drop in the place of the molecular sieves to account for the pressure loss. Industry experts also endorsed the use of a pumped LOX cycle for reasons described above and encouraged the inclusion of an argon recovery column in the model. After reviewing the model, the representatives from industry deemed the air separation unit "feasible" and "realistic [22]."

It is determined that the oxygen product from the air separation unit should be 99.5 percent or greater. Although oxygen used in coal gasification processes is 95 percent pure, the MATIANT cycle requires a greater purity. This is because of concerns about the ability to sequester impurities in the carbon dioxide stream. Carbon dioxide has

a boiling point of almost 200K (-73°C, -99°F) at 1atma, while oxygen, nitrogen and argon all boil below 90K (-183°C, -297°F) at the same pressure [23]. Personal communication with Howard Herzog of the Carbon Sequestration Initiative at the Massachusetts Institute of Technology notes that because oxygen is a non-condensable gas in the carbon dioxide, transporting it in pipes may be a problem. It is currently unknown if argon dissolves in liquid carbon dioxide. If not, it will cause the same problem [24]. It is believed that as pure an oxygen stream as possible should be produced and injected into the MATIANT cycle at the stoichiometric amounts relative to natural gas. This is indeed the path that was taken, as laid out in the Modeling chapter of this thesis.

Table A.2 on the following pages is a comprehensive table showing intermediate values that are used to obtain the first and second law efficiencies and heat rates shown in Chapter 4 of this thesis. The first four columns are taken from the HYSYS output of the case, while the fifth column is a summation of the previous three columns. The higher heating value of methane, not shown in the below table, is 890,330 $^{kJ}/_{kgmol}$. This value is used as laid out in Chapter 3 of this document.

Table A.2. Complete Table of Values for Parametric Studies

	fuel use (kgmol/s)	compressor power (MW)	turbine power (MW)	ASU power (MW)	net power (MW)	first law efficiency--HHV (%)	second law efficiency--(%)	heat rate (kJ/kWh)
base case	0.70	192.9	490.8	53.2	244.7	39.3	58.0	9154.4
fuel p=1379kPaa	0.70	197.3	493.1	53.2	242.6	39.0	57.7	9233.6
fuel p=689.5kPaa	0.70	199.5	495.3	53.2	242.6	39.0	57.5	9233.6
O2 T=24°C, p=344.7kPaa, no ASU	0.71	202.2	495.3	0	293.1	46.6	68.7	7718.6
O2 T=24°C, p=344.7kPaa	0.71	202.2	495.3	53.7	239.4	38.1	56.2	9450.0
O2 T=24°C, p=689.5kPaa, no ASU	0.71	199	494.3	0	295.3	47.0	69.4	7661.1
O2 T=24°C, p=689.5kPaa	0.71	199	494.3	53.7	241.6	38.4	56.8	9363.9
O2 T=24°C, no ASU	0.70	192.9	488.2	0	295.3	47.5	70.3	7585.7
O2 T=24°C	0.70	192.9	488.2	53.2	242.1	38.9	57.6	9252.7
Refrigeration	0.70	195	489.5	53.2	241.3	38.8	57.6	9283.3
Refrigeration Inter T=40°C	0.70	211.1	489.5	53.1	225.3	36.2	53.4	9942.6
Refrigeration Inter T=45°C	0.70	220.4	489.5	53.1	216	34.8	51.3	10346.0
Refrigeration Inter T=50°C	0.70	231	489.5	53.1	205.4	33.1	48.9	10879.9
Max T=~1460°C	0.69	176	483	52.2	254.8	41.7	58.1	8631.7
Max T=~1370°C	0.69	184.5	485.1	52.5	248.1	40.4	58.1	8914.9
Max T=~1330°C	0.70	190.8	491.8	53.3	247.7	39.7	58.1	9061.7
Max T=~1260°C	0.71	198.1	495.1	53.7	243.3	38.7	57.9	9295.1
Max T=~1225°C	0.70	201.7	494.2	53.6	238.9	38.1	57.7	9456.6

Table A.2. Continued

	fuel use (kgmol/s)	compressor power (MW)	turbine power (MW)	ASU power (MW)	net power (MW)	first law efficiency--HHV (%)	second law efficiency--(%)	heat rate (kJ/kWh)
Max T=~1150°C	0.72	213.9	500.9	54.4	232.6	36.5	57.6	9858.4
Inter T=50°C	0.71	218.7	495.4	53.7	223	35.5	52.6	10137.0
Inter T=45°C	0.70	213.6	493.4	53.5	226.3	36.2	53.4	9953.8
Inter T=40°C	0.70	207	493.4	53.5	232.9	37.2	55.0	9671.7
Inter T=35°C	0.70	201	493.3	53.5	238.8	38.2	56.4	9432.7
Simple Cycle	0.86	197.6	440.8	0	243.2	31.7	76.7	11348.8
Five Compressor Stages	0.70	182.2	490.8	53.2	255.4	41.0	60.5	8770.8
Max P=20000kPaa	0.70	187.2	482.5	53.2	242.1	38.9	58.1	9252.7
Max P=30000kPaa	0.70	198.2	490.8	53.2	239.4	38.5	56.5	9360.7

Table A.3 below contains conversions from metric units to English units of certain thermodynamic properties and other values that are crucial in this thesis. Temperature and pressure units in this thesis are shown in both English and metric units, except in tables and figures.

Table A.3. Conversions from Metric to English Units

Unit	Given	Multiply By	To Convert To
Molar Flow Rate	kgmol/s	2.2	lbmol/s
Enthalpy	kJ/kgmol	0.431	Btu/lbmol
Entropy	kJ/kgmol – ° C	0.239	Btu/lbmol – ° F
Moles	kgmol (or lbmol)	Molecular Weight	kg (or lb)
Power	MW	1341	hp
Heat Rate	kJ/kW – hr	1.27	Btu/hp – hr

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VITA

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